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JARKKO TISSARI

Fine Particle Emissions from Residential Wood Combustion

Doctoral dissertation

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Abstract

Residential wood combustion (RWC) appliances have the high probability of incomplete combustion, producing e.g. fine particles and hazardous organic compounds. In this thesis, the fine particle number and mass emissions, particle composition and morphology, and gas emissions were investigated from the modern (MMH) and conventional masonry heaters (CMH), sauna stoves (SS) and pellet burner. The investigation was based on laboratory and field experiments applying extensive and unique particle sampling methods.

The appliance type, fuel and operational practices were found to affect clearly the fine particle emissions. In good combustion conditions (e.g. in pellet combustion), the fine particle mass (PM_1) emission factors were low, typically below 0.3 g kg^{-1}, and over 90% of the PM_1 consisted of inorganic compounds (i.e "fine ash"). From the CMH the typical PM_1 values were 1.6–1.8 g kg^{-1}, and from the SS 2.7–5.0 g kg^{-1}, but were strongly dependent on operational practices. The smouldering combustion in CMH increased PM_1 emission up to 10 g kg^{-1}. The good secondary combustion in the MMH reduced the particle organic matter (POM) and gaseous emissions, but not substantially the elemental carbon (EC, i.e. soot) emission, and the typical PM_1 values were 0.7–0.8 g kg^{-1}.

The particle number emissions were high, varying from 1.0×10^{14} kg^{-1} to 42×10^{14} kg^{-1} and did not correspond with the completition of combustion. The particle number distributions were mainly dominated by ultrafine (<100 nm) particles, but varied dependent on combustion conditions. The electronmicroscopy analyses showed that ultrafine particles were composed mainly of K, S and Zn. From the smouldering combustion, particles were composed mainly of carbon compounds and they had a closed sintered-like structure, due to organic matter on the particles.

Controlling the gasification rate via the primary air supply, log and batch size, as well as fuel moisture content, is important for the reduction of emissions in batch combustion appliances. To reduce emissions of sauna stoves, the combustion technique or secondary removal techniques must be developed.

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I also thank my co-authors, Olli Sippula MSc and Kati Hytönen MSc from the University of Kuopio, Jussi Lyyränen PhD, and Unto Tapper PhD, of VTT, the Technical Research Centre of Finland, and all other colleagues at the Finnish Meteorological Institute, the National Public Health Institute, and the TTS Research, for their wonderful co-operation during the work. I wish to thank all my colleagues in the Fine Particle and Aerosol Technology Laboratory. In addition, special thanks go to Pentti Willman for his assistance in laboratory analyses, and to Anita Kajander for her help.

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Kuopio, August 2008

Jarkko Tissari

List of acronyms and definitions

CMH	Conventional masonry heater. Masonry heater with traditional rift grate.
Coarse fly ash	Coarse (> 1 µm) low volatile ash compounds that are ejected from the fuel bed into flue gas.
DLPI	Dekati low pressure impactor
DR	Dilution ratio
DT	Dilution tunnel
EC	Elemental carbon
ED	Ejector diluter
ELPI	Electrical low pressure impactor
Fine ash	Volatile ash compounds (below size of 1 µm, primarily alkali metal compounds) that are volatilized during combustion.
FMPS	Fast mobility particle sizer
GMD	Geometric mean diameter
MH	Masonry heater. Heavy (>800 kg) wood combustion appliance which stores energy released from combustion to the massive structure of heater and slowly radiates into indoor air.
MMH	Modern masonry heater. Masonry heater with unique grate design.
MMD	Mass mean diameter
NC	Normal combustion. The case where the CMH was used with the best available operational practice for the heater.
OGC	Organic gaseous compounds measured with flame ionization detector (FID).
OC	Organic carbon
PM	Particle mass or particulate matter
PM_x	Particle mass below aerodynamic size of x µm.
POM	Particle organic matter: determined by converting the mass of the organic carbon (OC) to the total mass of the organic compound (POM) using a factor that accounts for the oxygen, hydrogen, and some other elements present. The scale factor of 1.8 was used in this thesis.

PRD	Porous tube diluter
RWC	Residential wood combustion
Soot	Complex mixture consisting mainly of amorphous elemental carbon (EC) and organic material. Typically the blacker the smoke is, the higher is the elemental carbon content.
S or WS	Stove. Light wood combustion appliances that is free-standing, not storing- or semi-storing wood heaters usually made of steel.
SC	Smouldering combustion. Generally, highly incomplete combustion caused by overall lack of oxygen.
SEM	Scanning electron microscopy
SS	Sauna stove. Heaters used for heating sauna rooms. They are typically made of steel and have no means of preserving the heat produced.
TEM	Transmission electron microscopy

List of publications

This thesis is based on four original publications referred to the text by their Roman numerals (**I–IV**).

Paper I: Tissari, J., Hytönen, K., Sippula, O., Jokiniemi, J. (2008) The effects of operating conditions on emissions from masonry heaters and sauna stoves. Accepted to *Biomass & Bioenergy*.

Paper II: Tissari, J., Lyyränen, J., Hytönen, K., Sippula, O., Tapper, U., Frey, A., Saarnio, K., Pennanen, A., Hillamo, R., Salonen, R., Hirvonen, M.-R., Jokiniemi, J. (2008) Fine particle and gaseous emissions from normal and smouldering wood combustion fired in a conventional masonry heater. Accepted to *Atmospheric Environment.*

Paper III: Tissari, J., Hytönen, K., Lyyränen, J., Jokiniemi, J. (2007) A novel field measurement method for determining fine particle and gas emissions from residential wood combustion. *Atmospheric Environment* **41**, 8330–8344.

Paper IV: Tissari, J., Sippula, O., Kouki, J., Vuorio, K., Jokiniemi, J. (2008) Fine particle and gas emissions from the combustion of agricultural fuels fired in a 20 kW burner. *Energy & Fuels* **22**, 2033–2042.

Author's contribution

The research reported in this thesis was mainly carried out at the Fine Particle and Aerosol Technology Laboratory of the University of Kuopio, Finland, during 2002–2008. Paper I is based on the experimental work to investigate the emissions from masonry heaters and sauna stoves. The experiments were constructed mainly by the author and carried out with the help of K. Hytönen MSc and O. Sippula MSc (Tech.) under the supervision of Prof. T. Raunemaa and Prof. J. Jokiniemi. The data analysis and interpretation were performed by the author.

Papers II–IV were carried out under the supervision of Prof. J. Jokiniemi. Paper II characterised the fine particle emissions from a conventional masonry heater during smouldering and normal combustion conditions. The experiments described in Paper II were carried out by the author with the help of K. Hytönen MSc, J. Lyyränen PhD, A. Pennanen PhD and A. Frey MSc. In Paper II the scanning electron microscopy samples were collected by J. Lyyränen PhD and analysis was performed by U. Tapper PhD. The data analysis and interpretation were mainly performed by the author with the help of O. Sippula MSc (Tech.).

The field experiments from residential appliances described in Paper III were carried out by the author with the help of K. Hytönen MSc, J. Lyyränen PhD and T. Turrek MSc. The data analysis and interpretation were mainly performed by the author. The PAH sampling and analysis were carried out by K. Hytönen MSc.

The wood pellet and agricultural fuel combustion experiments described in Paper IV were carried out at the TTS Research, Rajamäki, Finland. The combustion experiments were mainly arranged by J. Kouki and K. Vuorio. The emission measurements were carried out by the author and O. Sippula MSc (Tech.). The data analysis and calculation of results were carried out by the author. The interpretation of data was performed by the author with the help of O. Sippula MSc (Tech.).

The author was responsible for writing in all of the Papers.

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1 Introduction

Fine particles ($PM_{2.5}$: Particle Mass below aerodynamic size of 2.5 µm) are one of the most important pollutant in outdoor air (Pope and Dockery, 2006). The impact of airborne particles on health is very varied, ranging from causing mild, short-lived symptoms to contributing to the onset or worsening of chronic conditions and premature death (Dockery *et al.*, 1993; Kappos *et al.*, 2004; Salonen and Pennanen, 2007). A safe threshold level for fine particle concentrations in urban air cannot yet be determined (WHO, 1994).

Residential wood combustion (RWC) for heat production has been assessed to be a major source of fine particle mass emissions, particulate polyaromatic hydrocarbons (PAHs) and certain gaseous pollutants such as volatile organic compounds (VOCs) throughout Europe (e.g. Olsson *et al.*, 1997; Christensen *et al.*, 1998; Salonen and Pennanen, 2007). In Finland, the main source of fine particles is long-range transport, whereas traffic, energy plants, industrial processes and residential wood combustion (RWC) are the most important stationary emission sources. A recent study reported that RWC accounted for 25% of the stationary combustion emissions in Finland in 2000, based on primary $PM_{2.5}$ (Karvosenoja *et al.*, 2008). On the other hand, it has been estimated that RWC can produce locally as much as 20–90% of the wintertime fine particle emissions (Muhlbaler Dasch, 1982; Boman *et al.*, 2003).

According to the latest studies, the health effects of inhaled aerosol particles from wood combustion may be more harmful than has previously been thought (Boman *et al.*, 2003; Naeher *et al.*, 2007). Health studies in residential areas with prevalent small-scale wood combustion have indicated that asthmatic subjects are vulnerable to this kind of air pollution (Larson and Koenig 1994; Boman *et al.* 2003). In many developing countries, wood combustion is a major source of energy for indoor cooking and heating, and epidemiological studies have reported, a high incidence of lung cancer among women who use stoves in China (Liu *et al.*, 1993; Pintos *et al.*, 1998). The small size of the particles may increase significantly the population's exposure to respiratory ailments and other health risks (Seaton *et al.*, 1995; Pope *et al.*, 2002).

On the other hand, it is well known that atmospheric aerosols influence climate (IPCC, 2007). Flaming combustion at high temperatures produces "sooty" smoke which strongly absorbs solar radiation and warms the atmosphere (Colbeck *et al.*, 1997). However, fine particles primarily cool the atmosphere, because smouldering combustion at low combustion temperatures produces an aerosol that predominantly scatters sunlight, and the fine particles form clouds that reflect sunlight back to space (e.g. Colbeck *et al.*, 1997). Furthermore, incomplete wood combustion produces methane and nitrogen-rich fuels N_2O that are the effective greenhouse gases (Seinfeld and Pandis, 1998). However, because biomass fuels are carbon dioxide (CO_2) neutral, according to different international requirements, the use of these renewable energy sources will be increased in the near future, in order to decrease the emissions of greenhouse gases. According to an EU agreement, the use of renewable energy in Finland has to increase from 28% to 38% by 2020. This also requires an increase in all kinds of wood energy.

The combustion conditions are very different in small-scale combustion appliances than in large power plants. In small combustion units, the local atmosphere and temperature vary considerably depending on the grate and burner. In addition, there are many different uncontrolled factors that also affect the combustion conditions. For example, numerous types and models of wood combustion appliances in use, and wood fuel can originate from several tree species. The operational practices of RWC also vary widely (e.g., fuel seasoning, combustion patterns, combustion rates, kindling approaches etc.) and often these practises are not well established from the emission point of view. Thus, the emissions from RWC have been demonstrated to be highly

variable (Nussbaumer, 2003; Johansson *et al.*, 2003; Johansson *et al.*, 2004; Sippula *et al.*, 2007a).

In most cases, small wood combustion appliances are not equipped with a flue gas filtering system. Because they also have a high probability of incomplete combustion, which leads to the production of fine particles and hazardous organic compounds, RWC cause air quality problems locally in densely populated areas where wood combustion is common (Glasius *et al.*, 2006). The dispersion and the dilution of the particles are dependent on the prevailling weather conditions (Boman *et al.*, 2003b). Most problems occur during winter periods with stagnant weather conditions, and wood combustion can result in local particle levels comparable to heavily trafficked streets (Glasius *et al.*, 2006). Because of varying outdoor temperatures, the use of wood combustion appliances is seasonal and air quality problems occur in episodes (e.g. Kukkonen *et al.*, 2005). Emission height in RWC is usually only a few meters above the ground. Therefore emissions do not have much time to dilute, oxidize or react chemically before people who live in the neighbourhood of wood combustion are exposed.

Primarily due to their health effects, there is a need to decrease the particle and gaseous emissions from wood combustion in small scale appliances. Because the mechanisms of the health effects are not yet known exactly, studying both fine particle physical and chemical properties is important (Lightly *et al.*, 2000). These properties (e.g. particle size and morphology, number and mass concentration, chemical composition) are dependent on combustion conditions. In future, there will be more stringent emission regulations which will also consider emissions from residential combustion. In many cases, flue gas filtering systems are still not economically feasible in small scale appliances, and on the other hand there is a large potential to decrease emissions by developing the combustion technology itself. Thus, there is actual need to get detailed information from the particle and gas emissions in small scale appliances. This enables the development of low emission combustion techniques and increases understanding on the relation between certain health and climate effects to put right measures to reduce harmful effects of from RWC.

Generally, there are several studies on emissions from wood-fired appliances (e.g. Hedberg et al., 2002; Johansson *et al.*, 2004; Koyuncu and Pinar, 2007). However, there is lack in the present knowledge, especially concerning fine particle emissions and their composition during different combustion conditions. Moreover, there are not any studies from emissions in the Finnish context. In addition, due to the difference in climate conditions and construction, the combustion appliances and operational practices are different in Finland than in many other countries and thus, the present knowledge can not be directly generalized to the Finnish context.

In this thesis, a general picture on the significance of different factors influencing the fine particle emissions from RWC appliances was obtained. This thesis was focused on the chemical and physical composition of fine particle and gas emissions during different combustion conditions from real RWC appliances used in Finland, excluding the emissions of single organic compounds such as PAH and VOC. The investigation was based on laboratory and field experiments applying extensive and unique particle sampling methods. The literature review part of this thesis is concentrated on the formation of emissions in RWC and the combustion conditions in small-scale appliances.

2 Residential wood combustion

2.1 Composition of wood fuel

Fuel properties have an important effect on the combustion of solid fuel. In contrast to many other fuels, the volatile matter content of wood is high, typically 80% by dry weight, and that strongly affects the combustion. Wood fuel is composed primarily of carbon (C), oxygen (O) and hydrogen (H). The carbon content of dry wood is typically 47–52%, whereas the oxygen and hydrogen contents are 38–45% and 6.1–6.3%, respectively (Van Loo and Koppejan, 2008).

Structurally, wood is composed mainly of cellulose (40–45% of dry weight), hemicellulose (20–35%), lignin (15–30%), and to a lesser extent of extracts. The fibre walls of wood consist mainly of cellulose ($C_6H_{10}O_5$), which is a condensed polymer of glucose. Hemicellulose consists of various sugars such as glucose, which encases the cellulose fibers. Lignin (e.g. $C_{40}H_{44}O_{14}$) is a high molecular mass complex non-sugar polymer that gives strength to the wood fibre (Van Loo and Koppejan, 2008).

Wood fuel also contains other inorganic compounds that are bounded to the organic structure of wood. Nitrogen content is low, typically below 0.5%. Mineral content is typically below 0.5%. The main compounds are calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), sulphur (S), chlorine (Cl), phosphorus (P), iron (Fe), aluminium (Al) and zinc (Zn) (e.g. **Paper IV**, Table 1).

In addition, wood fuel always contains water. The water content of a dry wood pellet is about 6%, whereas the water content of wood logs is 10–30%, and that of wood chips is even higher, up to 60%.

2.2 Wood combustion process

Combustion is a reaction where fuel reacts with oxygen, and this chemical process produce heat energy. The combustion of fuel particle is composed of several combustion phases, e.g. drying and heating of fuel, pyrolysis, firing and combustion. The first phases need heat, whereas flaming combustion and combustion of residual char produces heat. In the combustion of wood fuels, the combustion reactions take place primarily between gaseous products but the combustion of residual char is composed particularly of reactions between gases and carbon in the surface of solid char.

2.2.1 Drying and pyrolysis

In the first phase, the fuel particle warm up to drying temperature, after which most of the water is vaporized. The drying of porous fuel particle is dependent on the fuel water content, the rate of heat transport and vapour pressures between fuel and the surrounding (Rogge *et al.*, 1998; Simoneit *et al.*, 1999; Van Loo and Koppejan, 2008).

Fuel temperature increases and the volatile hydrocarbons begin to vaporize when the surface of the fuel has dried enough. Pyrolysis is composed of several complex parallel and sequential chemical reactions. In pyrolysis, the fuel constituents start to hydrolyze, oxidize and dehydrate, and the large structures (e.g. cellulose, hemicellulose and lignin) degrade. During pyrolysis, many different gaseous and liquid products such as volatile organic compounds, water, CO_2, H_2 and carbon monoxide (CO) are formed (e.g. Rogge *et al.*, 1998; Simoneit *et al.*, 1999; Van Loo and Koppejan, 2008).

It has been observed that the devolatilization of wood starts, and devolatilization rate substantially increases, above the temperature of 200 °C (Van Loo and Koppejan, 2008). The decomposition of hemicellulose occurs at 200–350 °C, since cellulose decomposes at 250–450 °C. At 400 °C, most volatiles are gone and the devolatilization rate decreases rapidly. The lignin decomposes throughout the temperature range from 200 to 500 °C, but the main weight loss occurs at higher temperatures.

2.2.2 Combustion

The combustion gases kindle when the production of heat is higher than the heat losses to the environment. Typically, the products of pyrolysis burn as a diffusion flame round the fuel particle and produces heat also for the other pyrolysis reactions. The pyrolysis gases are oxidized in the interface of air and pyrolysis products. Because of the increased heat rate, the temperature of the fuel increases, and combustion accelerates until the production of pyrolysis gases slows down. During pyrolysis, the ratio of C/H in fuel increases, and the combustion of residual char starts; this is best described as the gradual oxidation of the reactive char (solid phase combustion) (e.g. Rogge *et al.*, 1998; Simoneit *et al.*, 1999).

Although the residual char content from biomass combustion is typically only 10–30% by dry weight, the energy produced is 25–50% of the total energy produced during combustion. The combustion of residual char is composed of both reactions between gaseous products and particularly reactions between gases and the surface of solid char. The diffusion rate of oxygen to the surface of char is very slow. This restricts the combustion rate of residual char, so the combustion of char is the slowest phase. Typically for example in the wood log combustion, char combustion begin already during pyrolysis. In addition, the combustion reactions occur also inside the residual char, and thus the porosity of char strongly affects the combustion time. (e.g. Flagan and Seinfeld, 1988; Van Loo and Koppejan, 2008).

2.2.3 Batch and continuous combustion

In RWC appliances, the combustion process can be a continuous or batch type process. With continuous fuel feeding, different combustion phases occur in the fuel layer, and combustion is steady, and can be better controlled than in batch combustion appliances. However, the combustion process can be unstable especially in the interference, cleaning, on-off using and low load combustion phases in continuous combustion appliances. In batch burning appliances, there is a distinct separation between combustion phases in position and time (Van Loo and Koppejan, 2008). The combustion can be divided into three phases: (1) the firing phase; (2) the combustion phase; and (3) the burn out phase. Based on experience on combustion conditions during batch combustion, in this study, the combustion phases are defined as follows: The firing phase is defined as lasting from the ignition of the fire until the moment when the minimum oxygen concentration is reached (**Paper I**, Figure 2). This phase includes drying, warming and the initial part of the pyrolysis of the fuel batch. The combustion phase includes the strong and dying flaming combustion. The combustion phase is the period from the minimum oxygen concentration up to a concentration of 14%, and the burn out phase is from then on. In the next batch, all the combustion phases occur again sequentially.

2.3 Requirements for complete combustion

The most important parameters for complete combustion conditions are (1) a high combustion temperature, (2) a sufficient amount of combustion air supply, and (3) adequate mixing of combustion air and fuel gas (e.g. Nussbaumer, 2003; Van Loo and Koppejan, 2008).

2.3.1 Combustion temperature

The combustion temperature affects primarily the burn out of combustion compounds. The oxidation reactions are faster and more complete, and the combustion time shorter in high temperatures than at low ones. In RWC appliances, the heat can be transferred by conduction, convection or radiation. The heat capacity and density, thickness, insulation and surface properties of the material used in the firebox affect the combustion temperature. For example, the radiation loss through the glass door will be large per unit surface area, compared with the conductive heat loss through the combustion chamber walls per unit surface area (Van Loo and Koppejan, 2008). For complete combustion, it is necessary to minimize heat losses from the

combustion chamber. In light stoves, a higher combustion chamber temperature can be achieved by improving the insulation of the combustion chamber. The capability of heat storage (ceramic or soapstone material) in masonry heaters and brickwork in boilers enable higher combustion temperatures. In masonry heaters, the hot closed firebox surface reflects heat back into the flame and creates the gas turbulence needed for complete combustion. In open fireplaces, cookstoves or camp-fires, due to the lack of radiative heating, much heat is often lost to the surroundings and this restricts the combustion temperature and combustion rate (e.g. Van Loo and Koppejan, 2008).

In RWC appliances, there is normally an overall excess of oxygen to ensure a sufficient mixing of combustion air and fuel gas. However, the combustion temperature decreases as a function of the excess air ratio due mainly to the heating of inert nitrogen in the air. The temperature of the combustion chamber can be considerably increased by preheating the air. In addition, the vaporization of the fuel moisture uses energy released from the combustion process; it lowers the temperature in the combustion chamber, which slows down the combustion process (e.g. Van Loo and Koppejan, 2008).

2.3.2 Combustion air supply

A sufficient air supply is also very important for complete combustion (e.g. Van Loo and Koppejan, 2008). Although, a combustion process may have globally an excess of air, in many cases there may be locally deficiency of air due to poor mixing. An overall lack of oxygen leads the smouldering combustion conditions.

The gasification rate of wood is controlled mainly by the primary air supply, but the log and batch sizes (i.e. total area of wood logs) also strongly affect the gasification rate of wood in batch combustion. Thus, a restriction of the air supply and too large fuel batches in relation to the size of the air intakes, which are common operational errors in log-wood heating, cause an insufficiency of the air supply.

The addition of air in RWC appliances can be carried out by a forced or natural draught. The draught affects air flow rates to the combustion appliances and also the combustion conditions. In natural draught appliances, the chimney damper is used to control the flow conditions in the firebox, but too low and too high flow rates occur in practise. A too low draught leads to insufficient air and the dying of the fire. A too high draught leads to a lower combustion temperature due to the high excess air, or an increase in the gasification rate and an insufficiency of air, depending on the fuel surface area loaded in the firebox. In continuous combustion appliances, flue gas fans or air blowers are used to control the combustion process and draught conditions.

2.3.3 Mixing of combustion air and fuel gas

Complete combustion requires good mixing of secondary air and combustion gases, and a satisfactory residence time for the flue gases for oxidation (e.g. Stehler, 2000; Nussbaumer, 2003). Good mixing reduces the amount of air needed, providing a local and overall excess air ratio and higher combustion temperature. Inadequate mixing in the combustion chamber leads to local fuel-rich combustion zones and increases emissions.

Due to the high volatile matter content in wood fuel, complete secondary combustion is also important in wood combustion. In modern combustion appliances, the combustion air is supplied evenly in three stages to the firebox or burners. The primary air regulates the combustion rate, whereas the secondary and probable tertiary air enhances secondary combustion. Introduction of the heated secondary air into the top of the primary combustion chamber enhances the ignition of the combustion gases in the secondary combustion chamber. In modern boilers, O_2 or a CH (hydrocarbons) sensor are more and more often used to ensure good combustion conditions and a sufficient air supply (e.g. Stehler, 2000).

Particularly in the char combustion phase, the radical concentrations may be too low for complete combustion. Without radicals, the

combustion happens by the diffusion of oxygen to the surface of char, which is slow and increases CO emissions (e.g. Flagan and Seinfeld, 1988; Van Loo and Koppejan, 2008).

2.3.4 Operational parameters

In addition, many uncontrolled factors affect combustion conditions and emissions (Nussbaumer, 2003; Johansson *et al.*, 2003; Johansson *et al.*, 2004). The combustion of wood fuel is dependent on its chemical (heating value, reactivity), physical (heat capacity, heat conductivity) and structural (particle size, density, porosity) properties. For example, fuel density influences the combustion chamber volume to energy input ratio, and also the combustion characteristics and thermal behaviour of the fuel. Operational practices, e.g., fuel seasoning, the distribution of fuel inside the combustion chamber, combustion patterns, combustion rates, and kindling approaches, also affect emissions.

2.4 Residential combustion appliances

In many developing countries, biomass combustion in small appliances is a major source of energy for indoor cooking and heating (e.g. Viau *et al.*, 2000). For example, in India hundred of millions of households use biofuels for cooking energy (Venkataraman and Uma Maheswara Rao, 2001). On the other hand, biomass fuels are combusted in grate-fired boilers or co-fired in pulverized coal combustion from a few megawatts up to 1000 MW. In addition, large amounts of biomass burn uncontrolled, for example in natural fires (Robinson *et al.*, 2007; Jalava *et al.*, 2006). In Finland, wood is used mainly as an auxiliary heat source in one-family houses, and is combusted in masonry heaters and different types of stoves. Different forms of wood fuels are used, such as wood logs, densified logs and pellets, and wood chips.

The common types of RWC devices have been described by, for instance, Baxter *et al.* (2002) and Van Loo and Koppejan (2008). The most common RWC appliances can be divided into five categories: three types of batch combustion appliances: (1) masonry heaters, (2) wood stoves and (3) wood log boilers; and two types of continuous combustion appliances: (4) pellet burners and boilers, and (5) stoker burners.

2.4.1 Masonry heaters

Masonry heaters (**Paper I**, Figure 1a,b; **Paper III**, Figure 1) have a very high mass, typically from about 800 to 3000 kg, and can be up to 6000 kg. They are enclosed combustion appliances made of masonry products, a combination of masonry products and ceramic materials, or soapstone (Stehler, 2000). Others are covered with decorative tiles and were developed in the 1700s as the first efficient wood firing device in Sweden (Van Loo and Koppejan, 2008). In these heaters wood is combusted in a relatively short period of time and at high power, which means that the combustion rate and temperature are high. Typically, the heaters have an upright firebox with a glass door. In the contraflow (e.g. **Paper II**, Figure 2) system, the exhaust gas flows from the firebox to an upper-combustion chamber, and goes down through the ducts into the chimney from the bottom or top of the heater. The energy released (40 to 100 kWh) is efficiently stored (combustion efficiency typically 75–85%) in the large mass surrounding the firebox and the ducts. Masonry heaters produce both primary and supplemental heat, when the heat stored in the stone mass slowly radiates (at an average rate of 1–3 kW) into the indoor air for the next 1 to 2 days, so they are well suited for Nordic cold-climate conditions. Most of the heaters have a conventional (rift) grate, and are called conventional masonry heaters (CMH). In a Finnish modern masonry heater (MMH), in contrast to a CMH, the primary airflow is controlled and secondary air is directed to envelop the fuel batch (e.g. **Paper I**, Figure 1b). Baking ovens (**Paper III**, Figure 1), which are common in Finland, have a flat grate without rifts, and the combustion air is introduced through the oven door. There are also several combinations of baking ovens and MHs.

2.4.2 Wood stoves

Wood stoves (WS or S) are free-standing (mass <800 kg), enclosed, not-storing or semi-storing wood heaters usually made of steel, sometimes covered with ceramic materials or soapstone to increase heat storage. In Finland, they are used primarily for aesthetic effects and secondarily as supplementary heating sources in houses, and as the primary source of heat in summer cottages. In warmer countries they are used both as the primary source of residential heat and for supplementary heating. Stoves release heat by radiation and convection to their surroundings. Wood stoves control combustion or burn time by restricting the amount of air that can lead the smouldering combustion conditions. In modern appliances, secondary air is preheated and introduced outside the primary combustion zone, in order to get good secondary combustion. In many appliances, the combustion chamber is small and some are surrounded by ducts through which floor level air is drawn by natural convection, heated, and returned to the room (e.g. Van Loo and Koppejan, 2008).

In the USA, catalytic stoves are also used. These are equipped with a ceramic or metal honeycomb device, called a combustor or converter, which is coated with a noble metal such as platinum or palladium. The catalytic combustor is usually placed in the flue gas channel beyond the combustion chamber. The catalyst material reduces the ignition temperature of the unburned VOC and CO in the exhaust gases, thus augmenting their ignition and combustion at normal stove operating temperatures (EPA, 1996a; Van Loo and Koppejan, 2008).

In Finland, sauna rooms are heated by sauna stoves (SS: **Paper I**, Figure 1c; **Paper III**, Figure 1), which are made of steel and have no means of reserving the heat produced. The combustion technique is very simple. Only about half of the released energy can be stored in the stones on the stove and consequently the exhaust gas temperature is high. The momentary need of heating in the sauna room is very high, so SS are also operated at high power in a similar way to masonry heaters.

Open fire heaters (open fireplaces) typically have large fixed openings in front of the fire bed and dampers above the combustion area in the chimney to limit room air and heat losses when the fireplace is not being used. They have very low thermal efficiency; in worst cases they consume more energy than they produce. Inserts are nowadays used to update an existing fireplace to a cleaner-burning and more efficient heat source (EPA, 1996b; Houck and Tiegs, 1998; Van Loo and Koppejan, 2008).

Cookstoves are very common appliances used as a source of energy for indoor cooking and heating in many developing countries. They are very simple appliances, usually simple tripods or three-stone stoves, or portable metal or ceramic cookstoves with efficiency from 8 to 30 % (Oahn *et al.*, 1999).

2.4.3 Wood log boilers

Central boiler systems deliver heat into the radiator grid of a dwelling. In Finland, underfloor heating is the most common in new detached houses. Heat circulation pumps distribute the hot water to the radiators, and thermostats regulate the heating power in the rooms to be heated. The boilers, which are made of steel, can be divided into three categories according to airflow designs in combustion, such as updraught (also known as over-fire), downdraught (under-fire) and crossdraught boilers (Johansson *et al.*, 2004). The traditional updraught wood log boilers operate in a similar way as wood stoves and masonry heaters. The heat released in combustion is recovered with a heat exchanger and stored in the water space in the boiler. The most problematic are multi-fuel boilers, which can burn wood, oil, or pellets, but are primarily used for wood log combustion with an upgraught technique. Because of the small firebox and water space in the boiler, the use of multi-fuel boiler without a heat storage tank can lead to smouldering combustion conditions. Modern wood boilers are usually designed for downdraught or crossdraught combustion. Often they have a secondary combustion chamber, which is normally insulated with ceramics, and connected to storage tanks. In crossdraught boilers, because

the flue gas flow resistance is quite high, a flue gas fan is needed. Advanced control devices such as O_2 sensors, air control and staged air combustion are also used (Baxter *et al.*, 2002; Johansson *et al.*, 2004; Van Loo and Koppejan, 2008).

2.4.4 Pellet burners and boilers

Pellet burners can be installed separately in water-cooled multi-fuel boilers or updraught boilers, or integrated with boilers (Baxter *et al.*, 2002; Johansson *et al.*, 2004). Modern appliances have heat control in large power scale with O_2 sensors, movable grates, effective heat exhangers and large ash-boxes (Stehler, 2000). The feeding of pellets from the fuel tank to the burner is typically controlled by a fully automatic system connected to the burner automatics. In the burner, dispensing of pellets is typically done first with a separate feeding screw through the airtight rotary feeder and thereafter by a burner screw in the burner head. This enables fire-safe operation (**Paper IV**, Figure 2). The burners can be classified into three types according to the feeding principle: (1) top-feed burners (also known as gravity or dropping feed or overfeed), (2) under feed (bottom fed) burners, and (3) side feed (or horizontally fed) burners. Respectively, the burners can be classified also into four types according to the combustion principle: grate-, gasifier-, bowl-, and tube burner combustion. Normally, pellet boilers do not have heat storage tanks and the boiler is set at thermostat control, which results in a cyclic, intermittent operation of the pellet burner. Some burners operate with a pilot flame, and others have electrical ignition, during low load combustion (Johansson *et al.*, 2003).

Pellet stoves and pellet fireplace inserts look like wood stoves, but have active air flow systems (recycling of indoor air) and a unique grate design (pellet burner) in the firebox. They are thermostatically controlled, and most have different burn settings (Sippula *et al.*, 2007a).

2.4.5 Stoker burners

Stoker burners operate in a similar way to side feed pellet burners, but they have larger burner screws and thus are suitable for wood chip combustion. The flame burns horizontally in the small grate in the burner head. The burner is mounted partially inside the firebox of the boiler, and partially outside it. The fuel is fed according to the heat demand, and combustion air is introduced from one or several blowers (Van Loo and Koppejan, 2008).

3 Formation of emissions

In the complete combustion of hydrocarbons only CO_2 and H_2O are produced. In wood combustion, also unwanted combustion products are always produced, and so in addition to the main gas compounds N_2, CO_2, H_2O and O_2, flue gas also contains e.g. CO, H_2, partially combusted hydrocarbons, sulphur dioxide (SO_2), nitrogen oxides (NO_x), hydrogen cloride (HCl) and different solid or liquid particles. The first fine particles formed in wood combustion are soot particles, which are already formed in the flame from hydrocarbons. The volatilization of alkali metals from the fuel leads to the formation of fine fly ash particles and these also occur in complete combustion (Oser *et al.,* 2001; Boman *et al.,* 2004; Sippula *et al.,* 2007a,b). In addition, aerosol from biomass combustion may include liquid or tar-like parts, which are products from the gas-to-particle conversion of organic vapours in cooled flue gas. These heavy hydrocarbons may also condense onto existing particles (Pyykönen *et al.,* 2007) or form new particles by nucleation (Shi and Harrison, 1999). In RWC, the coarse particles are ejected mainly from bottom ash and formed from low volatile ash compounds and partially unburnt char (Flagan and Seinfeld, 1988; Wiinikka, 2005).

3.1 Formation of gaseous emissions and organic particles

In complete combustion, C, H and O in fuel form only CO_2 and H_2O. Water vapour forms when water evaporates from fuel or during hydrogen oxididation. CO_2 is not considered to be a greenhouse gas emission in biomass combustion because forests and plants recycle carbon dioxide when growing. Wood fuels also contain N, S and volatile mineral compounds. NO_x compounds in flue gas are formed mainly from fuel nitrogen. At high temperatures (over 1400 °C), NO_x is also formed from N_2 in combustion air, but this is unlikely in RWC. N_2O is a very efficient greenhouse gas (Seinfeld and Pandis, 1998), but N_2O emissions from biomass combustion are typically low (Van Loo and Koppejan, 2008). In addition, NO_x and volatile organic compounds take part in the formation of secondary organic aerosol (SOA) in the atmosphere (Presto *et al.,* 2005; Kleindienst *et al.,* 2006; Robinson *et al.,* 2007). Sulphur in fuel oxidizes to SO_x in combustion. SO_x and NO_x compounds are also involved in the formation of fine ash particles, and sulphur can form sulphuric acid (H_2SO_4). In addition, particularly from fuel with high chlorine content, gaseous HCl may form to a significant extent. In contrast to agricultural fuels, wood fuel contains only small amounts of N, S and volatile alkali metals, and thus NO_x, SO_2 and HCl emissions are typically low (Van Loo and Koppejan, 2008).

The combustion of wood fuels in small-scale appliances is always partially incomplete due to local incomplete combustion conditions around the flame, low combustion temperatures, an insufficient air supply or poor mixing of combustion gases and air. As a result, CO and volatile hydrocarbon emissions are formed. In batch combustion, when char combustion begins, the combustion chamber temperature decreases, which leads in most cases to a level below that sufficient for the complete oxidation of CO. If the combustion is highly incomplete, heavy complex organic compounds are released to the flue gas. Poor combustion conditions can also be associated with natural fires that are a large source of organic matter in the atmosphere (e.g. Robinson *et al.,* 2007).

Organic compounds can occur as both gaseous and solid particles. They are typically divided according to their boiling points into very volatile (VVOC), volatile (VOC) and semivolatile organic carbon (SVOC) combounds and particle phase compounds (POM, particle organic matter) (Tucker, 2001) or into the corresponding functional group of molecular structure (alkanes, alkenes, aromatics etc.). Incomplete biomass combustion produces hundreds of different organic compounds (e.g. Rogge *et al.,* 1998; McDonald *et al.,* 2000; Lee *et al.,* 2005; Mazzoleni *et al.,* 2007; Alfarra *et al.,* 2007). One of the most important VOC from

biomass combustion is methane (CH_4) (Johansson *et al.,* 2004), which is also a very strong greenhouse gas. The warming effect of CH_4 is 21-fold that of CO_2 (Seinfeld and Pandis, 1998). Polycyclic aromatic hydrocarbons (PAH) are formed in the flame in local fuel-rich areas when hydrocarbons polymerize instead of oxidizing (Flagan and Seinfeld, 1988). In RWC, PAH compounds may also form from light organic compounds or from incomplete combustion of pyrolysis gases.

The particle formation mechanisms are shown in Figure 1. Aerosol from incomplete wood combustion may contain liquid or tar-like parts, which are products from the gas-to-particle conversion of organic vapours in cooled flue gas, usually far below the temperature of 500 °C (Figure 1, line 4). Depending on environmental conditions, organic compounds can be present in liquid or gaseous form. Heavy hydrocarbons may condense onto existing particles (Pyykönen *et al.*, 2007) or form new particles by nucleation (Shi and Harrison, 1999). If there are pre-existing particles in flue gas, it has been previously reported (Pyykönen *et al.,* 2007) that hydrocarbons condense onto existing particles rather than forming new particles by nucleation. The condensation of particles continues in the chimney and atmosphere when the combustion aerosol cools and is diluted. Evaporation and oxidation of organic aerosol is probable in the atmosphere (Robinson *et al.,* 2007). Thus, the particle properties of fresh RWC aerosol in winter are different from those of aged aerosol especially in summertime.

3.2 Formation of soot particles

Soot particles are formed mainly in the flame from hydrocarbons. The soot formation mechanisms are complex, and although there are several studies of the formation of soot particles, they are not yet well understood (e.g. Bockhorn, 1994; D'Anna *et al.*, 1994; Ishiguro *et al.*, 1997; Koziński and Saade, 1998). Most soot particles form in the fuel-rich zone inside a diffusion flame and grow rather than oxidize to CO or CO_2. Because of the insufficient mixing of combustion gases and air in RWC, the flame zone always contains fuel-rich areas even in the presence of overall excess air during combustion.

In the first step of soot formation, PAH compounds polymerize (Figure 1, line 1). In the next step, the size of PAH compounds increases and high PAH levels are reached. As a result, typically about 1–2 nm soot nuclei are produced by nucleation. After this, the nuclei increase by surface reactions and coagulation, and form about 10 nm core particles. More PAH compounds are bonded to the surface of core particles by surface reactions and this leads to the formation of primary soot particles (e.g. Bockhorn, 1994; D'Anna *et al.,* 1994; Ishiguro *et al.,* 1997).

It has been observed that the primary spherules are composed of lamella-like crystallites (Ishiguro *et al.,* 1997). The structure of these crystallites resembles that of graphite. In the outer shell of these spherules the crystallite structure is directed according to the shape of the surface, but in the spherules they are randomly arrayed. The formation of the outer shell of soot spherules and the agglomeration of spherules are parallel and simultaneous. The surface of a spherule is composed of very stable elemental carbon (EC) (Ishiguro *et al.*, 1997).

The number concentration of carbon spherules in the flame is extremely high and thus the formation rate of soot agglomerates is also high. Most of the soot particles burn in the oxygen-rich zone in the flame (Amann and Siegla, 1982; Wiinikka, 2005), but a minor part of the soot particles is released as agglomerates composed of about 30–50 nm solid carbon spherules (Figure 1, line 1). The extent of soot oxidation determines the size and number of the soot particles released.

Both the combustion conditions and the quality of gaseous compounds influence soot formation (Bartok *et al.,* 1991). The effect of temperature/heat input and oxygen/local mixing conditions appear to be important within both the pre-particle chemistry, responsible for the formation of incipient soot particles, and the soot surface-mass growth (Koziński and Saade, 1998). The oxygen content of dry wood is about 40%. In the pyrolyzation zone of the diffusion flame, the oxygen may increase the soot formation because it catalyses pyrolysis reactions more than do fuels

that contain no oxygen (Flagan and Seinfeld, 1988).

3.3 Formation of ash particles

In good combustion conditions, fine particle emissions are formed mainly by the vaporization of ash-forming elements from the wood fuel (Sippula *et al.,* 2007a,b; Figure 1, line 2). The formation of fine ash particles begin by homogenous nucleation, when the temperature decreases after the flame, and the vapour pressure of ash species also decreases (Jokiniemi *et al.,* 1994; Boman *et al.,* 2004). The vaporization is dependent on the chemical composition of the wood and the reactions of inorganic species (Olsson *et al.,* 1997; Davidsson *et al.,* 2002; Knudsen *et al.,* 2004; Sippula *et al.,* 2007a). Most mineral compounds are bound to the organic structure of biomass fuels and are easily released during the pyrolysis of fuel. The combustion temperature has an important influence on vaporization, so that greater amounts of ash particles are released at high temperatures than at low ones (Davidsson *et al.,* 2002; Knudsen *et al.,* 2004).

In wood fuels, potassium, sulphur, chlorine and sodium are very volatile. Further, in the reducing area of flame, species that have lower vapour pressure such as zinc and calcium may also volatilize (Knudsen *et al.,* 2004). In wood combustion, the fine fly ash is composed mainly of potassium compounds such as potassium sulphate (K_2SO_4), potassium chloride (KCl), potassium hydroxide (KOH) and potassium carbonate (K_2CO_3) (Christensen *et al.,* 1998; Valmari *et al.,* 1998; Silva *et al.,* 1999; Boman *et al.,* 2004; Sippula *et al.,* 2007a).

The release of alkali metals is influenced mainly by the fuel chlorine, sulphur and different sorbent mineral concentrations. High chlorine content has been found to enhance the release of alkali metals due to the formation of volatile alkali metal chlorides (Olsson *et al.,* 1997; Knudsen *et al.,* 2004). Knudsen et al. (2004) observed that the ratio of molar ratio of K/Si and Cl/K is important for alkali emissions. If there are silicates present, the aluminium and silicon compounds can react with potassium, forming more stable compounds (Jensen *et al.,* 2000; Davidsson *et al.,* 2002). Thus, a low K/Si ratio has been observed to limit the release of potassium. A high Cl/K ratio increases the release of alkali metals, since the chlorine prevents the potassium from combining with silicates and instead favours high vapour pressure volatile formation (Dayton *et al.,* 1999; Knudsen *et al.,* 2004). In contrast, a sufficient amount of sulphur in the fuel may inhibit the effect of chlorine throughout a sulfation reaction, in which the alkali metal chloride is converted to less volatile alkali metal sulphate (Sippula *et al.,* 2008). Further, sulfation of other alkali metal species such as hydroxides may decrease the release of alkali metals.

Very high fuel ash content in agricultural biomass, for example, may lead to operational problems such as fouling, slagging and corrosion of heat transfer surfaces in boilers, which reduce efficiency, and may even lead to costly shutdowns and repairs (Dayton *et al.,* 1995; Blander and Pelton, 1997; Davidsson *et al.,* 2002; Lindström *et al.,* 2007).

The coarse (~1–10 µm) particles occurring in biomass combustion are formed from low volatile ash compounds and partially are unburnt char (Figure 1, line 3). At low temperatures, large ash agglomerates are formed by agglomeration, but in sufficiently high temperatures ash compounds may melt and form regular ash droplets (Flagan and Seinfeld, 1988). Super coarse particles (>10 µm) are formed from residual fly ash particles that are ejected from the fuel bed and carried upwards by the gas (Wiinikka, 2005).

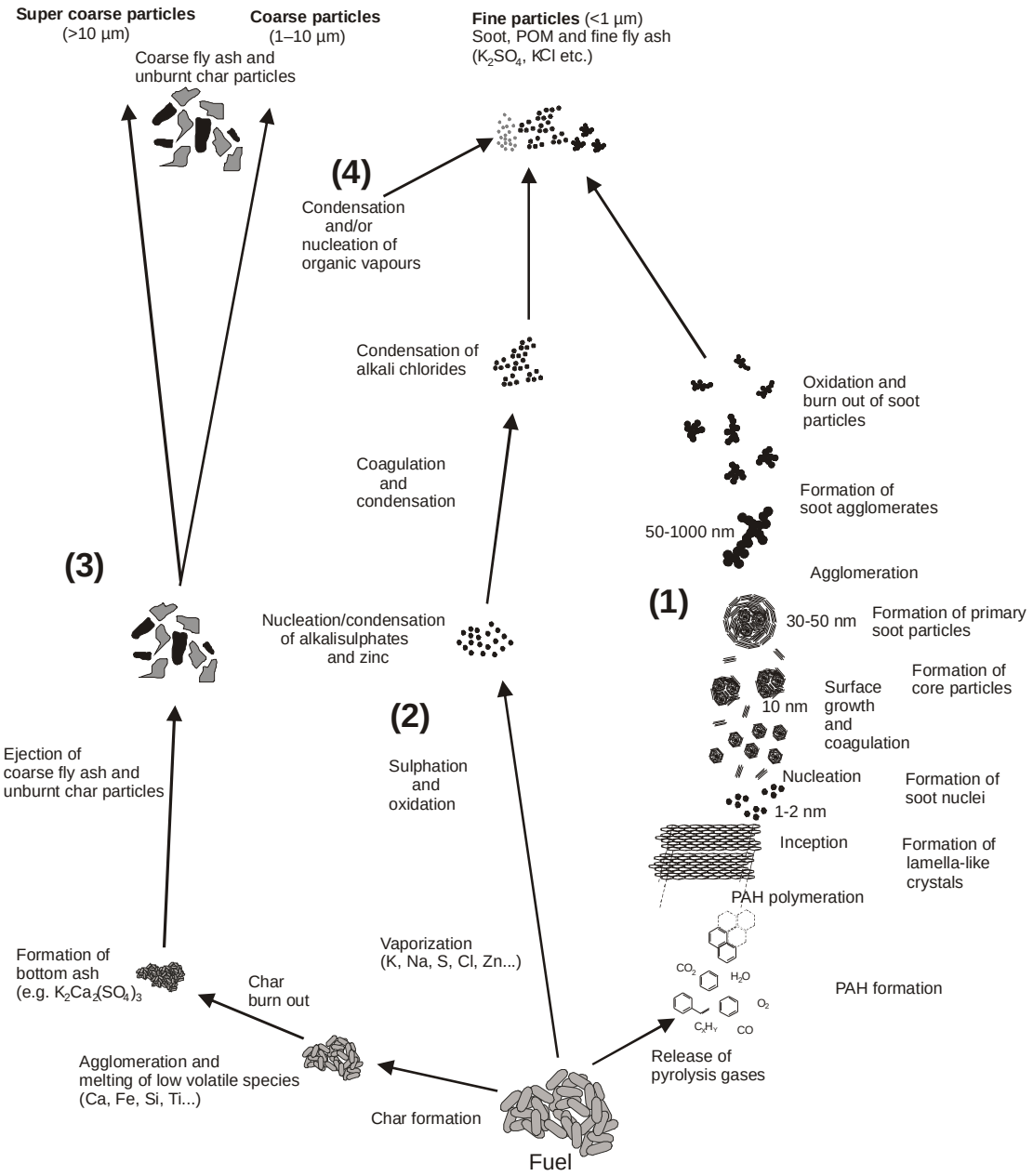


Figure 1. Illustration of the soot formation process (1), fine ash (2), coarse particles (3) and particle organic matter (POM) (4) during residential wood combustion according to Wiinikka (2005), Ishiguro *et al.* (1997) and Bockhorn (1994).

4 Aims of this study

The objective of this study was to assess the role of different factors influencing fine particle emissions from RWC. The main factors studied were fuel, combustion appliances, operational practices, and measurement methods. The investigation was based on laboratory and field experiments applying extensive quantity and quality characterisation of gas and particle species and unique particle sampling methods.

The specific aims of the study were:

- To study the influence of combustion phase on emissions (**Paper I**).
- To characterise the fine particles in relation to combustion appliance and combustion conditions (**Papers I–IV**).
- To clarify how operational practices affect emissions from Finnish appliances (**Papers I–III**).
- To determine the effect of biomass fuel properties on fine particle and gas emissions from a residential burner (**Paper IV**).
- To define emission factors for the most common Finnish heaters, to compare the results with those of other studies, and to provide uncertainty ranges of the emission factors used in emission inventories (**Papers I–IV**).

5 Measurement methods

The measurement of fine particles from RWC appliances is very challenging. The particle size range is very large, and the flue gas contains particles that vary from nanometers to micrometers in size. In addition, fine particles occur in three states in the flue gas: soot, inorganic ash or organic species, which may occur in the gas phase prior to sampling and nucleates or condenses during sampling. Several measurement devices have to be used if both the physical and chemical properties of fine particles are to be measured. Because of the variable and at least temporarily high vapour and particle concentration and high temperature in the flue gas, the sample gas has to be diluted before it is led to the measurement devices. The optimal dilution ratio (DR) varies between different devices.

In this chapter, the combustion arrangements and the measurement techniques and devices that were used are introduced. The measured appliances and combustion procedures have been introduced in **Papers I–IV**. The experiments are summarized in Table 1.

5.1 Combustion arrangements, particle sampling and dilution

Laboratory measurements. In the laboratory combustion experiments in the batch combustion (**Papers I–II**), the appliance was situated on a scale to enable the measurement of fuel mass flow (Figure 2). To mimic a natural draught, the combustion gases were led through an externally insulated steel stack placed below a hood. The draught in the stack was adjusted using a flue gas fan, changing the location of the hood, and with a damper mimicking natural draught conditions

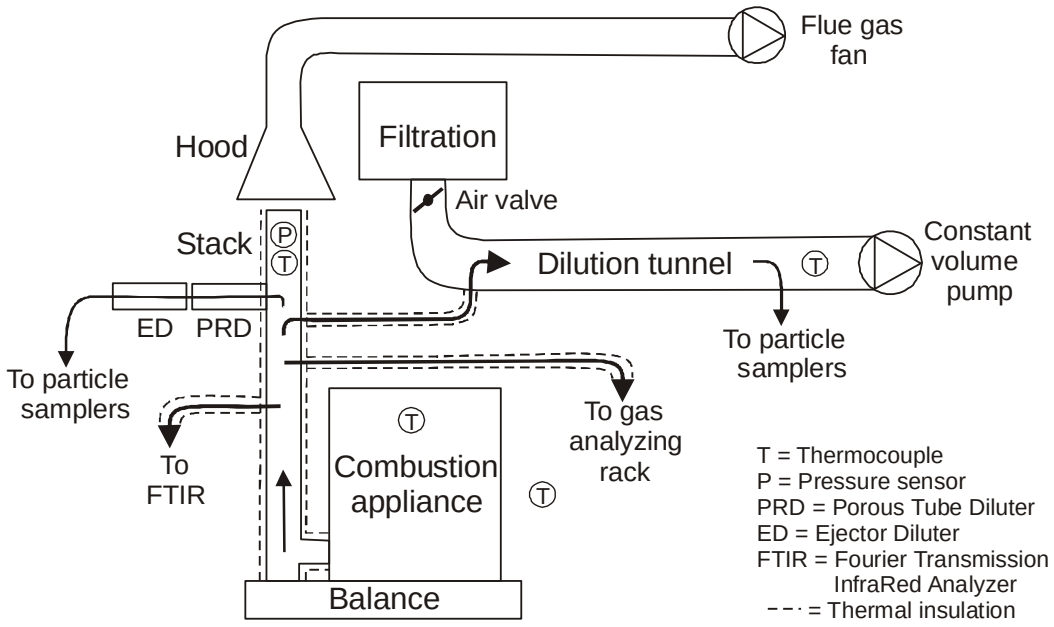


Figure 2. Experimental set-up of the fine particle and gas measurement from the RWC appliance. The dilution tunnel method and porous tube diluter with ejector diluter are parallel techniques for fine particle sampling and dilution. The used particle samplers are shown in chapters 5.2–5.6.

Before particle measurement, the sample flow was diluted in a dilution tunnel (DT) or a porous tube diluter (PRD) with an ejector diluter (ED, Dekati Ltd.). In the dilution tunnel method the dilution air was filtered in three stages, where a pre-filter removes coarse particles, a chemical filter removes hydrocarbons and nitrogen oxides, and a post-filter removes fine particles. A partial flow from the stack was led through an externally insulated 12 mm steel pipe to the dilution tunnel by the negative pressure in the tunnel.

The total air flow in the tunnel was adjusted with a constant volume pump (flow rate 0–1200 m^3 hr^{-1}) and the low pressure of the tunnel was controlled with an air valve situated after the filters, giving a typical DR of 50 to 300. In two of the laboratory combustion tests, EDs were used (Table 1). This kind of dilution is discussed in more detail in Lyyränen *et al.* (2004) and Wierzbicka *et al.* (2005).

Field measurement. In the field experiments (**Paper III**), the measurement devices were installed inside a box (volume 1.4 m^3). This box was heated in a van about 1.5 hours before and during the measurements with a thermostat-controlled heater (2 kW), and was elevated near the chimney with a telehandler. The sampling probe was situated in the center of the chimney (at a depth of about 30 cm). Electricity was produced by a 32 kW diesel generator and pressurized air by a compressor (both on the ground).

For particle measurements, a partial flow from the stack was led through an externally insulated 8 mm steel pipe connected to a special sampling probe with a 10 µm pre-cyclone. The sample flow was diluted in two steps. The first dilution, with filtered (particle-, hydrocarbon- and water-free) and heated (180 °C) air, took place in the PRD to minimize particle losses and transformation (Lyyränen *et al.*, 2004). The sample was further diluted with the ED to stabilize the sample flow through the whole measurement system and to ensure good mixing with dilution air, giving a total (typical) DR of 30–70. This particle measurement system was used in the measurements in **Papers III** and **IV**. Temperatures were monitored continuously from the combustion appliance, exhaust gas, particle sample lines, dilution tunnel and laboratory room air using thermocouples. In addition, other parameters, such as draught, was monitored.

5.2 Particle number and number size distribution measurements

Particle number emissions and number size distributions were measured in real time with an Electrical Low Pressure Impactor (ELPI, Dekati Ltd.; Keskinen *et al.*, 1992), and a Fast Mobility Particle Sizer (FMPS, TSI 3091). In the ELPI, the particles are first charged and then enter a cascade low pressure impactor with electrically insulated collection stages. The particles are collected in the different impactor stages according to their aerodynamic diameter, and the electric charge carried by the particles into each impactor stage is measured in real time by sensitive multichannel electrometers. This measured current signal is directly proportional to the particle active surface area and aerodynamic size (Keskinen *et al.*, 1992). The active surface area can then be converted to particle number concentration. Because of its wide particle size range (7 nm to 10 µm) and fast response time, the ELPI is a suitable measurement instrument for the analysis of unstable concentrations and size distributions in residential combustion (e.g. Hays *et al.*, 2003; Johansson *et al.*, 2004), and it is also widely used in the measurement of particle emissions from motor vehicles (e.g. Ahlvik *et al.*, 1998; Maricq *et al.*, 1999; Tsukamoto *et al.*, 2000) and power plants (e.g. Moisio, 1999). In this study, both 10 and 30 lpm flow rates were used. The sintered impactor stages were in most of the measurements.

In the FMPS, particles are positively charged to a predictable level using a corona charger. The charged particles are then introduced to the measurement region near the center of a high voltage electrode column and transported down the column via HEPA-filtered sheath air. A positive voltage is applied to the electrode, which creates an electric field that repels the particles outward according to their electrical mobility. Comparable older systems, a DMPS (Differential mobility particle sizer) and

an SMPS (scanning mobility particle sizer), have been widely used in atmosphere and combustion studies (e.g. Gaegauf *et al.*, 2001; Wierzbicka *et al.*, 2005). In the FMPS, charged particles strike the respective low-noise electrometers and transfer their charge. A particle with high electrical mobility strikes an electrometer near the top, whereas a particle with lower electrical mobility strikes an electrometer lower in the stack. This system produces particle size distribution measurements with one-second resolution. The FMPS measures particles in the submicron range from 5.6 to 560 nm. The size range is smaller than in the ELPI, but the number of size channels is higher, which gives better resolution especially for ultrafine particles. The FMPS operates at a high flow rate (10 lpm) to minimize diffusion losses of ultrafine and nanoparticles. It operates at ambient pressure to prevent evaporation of volatile particles.

The FMPS is also suitable for studies of transient emission from stacks, boilers, and wood burners, but it has not been used earlier in such studies. Because the ELPI is widely used in particle studies and it gives a wide particle size range, while the FMPS gives a good resolution for ultrafine particles, the combination of the FMPS and the ELPI gives a good picture of the particle number concentration and number size distributions presented in this thesis.

5.3 Particle mass and mass size distribution measurements

In RWC, the obtained emission factor and chemical composition of the particle mass is strongly dependent on the measurement technique used. The most important question is, whether the sampler collects organic material or not (e.g. Hildemann *et al.*, 1989). The effect of the measurement technique on emission factors is discussed in more detail in chapter 6.3.

The PM_1 samples were collected on filters from diluted gas using a pre-impactor (Dekati Ltd.) with a cut-off size of 1 µm to ensure the removal of coarse particles before the filter holders. The PM_1 samples for gravimetric and elemental analyses were collected on 47 mm Teflon membrane filters (polytetrafluoroethylene (PTFE)) (Gelman Scientific, Teflo). The samples for organic and elemental carbon analysis were collected in two parallel lines on 47 mm quartz fiber filters (Pallflex, Tissuequartz). Both lines had a quartz backup filter, to correct a positive sampling artefact from the adsorption of gaseous organic compounds on quartz fibre filter material (McDow and Huntzicker, 1990).

Particle mass size distributions were measured using a Dekati Low Pressure Impactor (DLPI, Dekati Ltd.). This cascade impactor classifies airborne particles into 13 size fractions. The particles are collected on 25 mm collection substrates that are weighed before and after measurement to obtain a gravimetric size distribution of the particles. The DLPI impactor has the same design as the impactor used in the ELPI. Low-pressure cascade impactors are widely used in combustion studies (e.g. Kauppinen and Pakkanen, 1990; Johansson *et al.*, 2003; Pagels *et al.*, 2003; Lillieblad *et al.*, 2004; Wierzbicka *et al.*, 2005; Wang *et al.*, 2007). In this study, the DLPI was used with a flow rate of 10 lpm and a cut-off size ranging from 28 nm to 9.84 µm with greased Al-foils as collection substrates.

The filters and Al-foils for gravimetric analysis were kept for 24 h at a constant temperature of 20 °C and a relative humidity of 40% before weighing, and were weighed using a microbalance (Mettler Toledo MT1) of 1 µg sensitivity. The weighing procedure is presented in detail in Tiitta *et al.* (2002).

5.4 Analysis of particle chemical composition

There are several different methods and protocols to determine organic carbon (OC) and elemental carbon (EC) concentrations of particle matter. The results are affected by thermal evolution temperatures, pyrolysis corrections, analysis atmosphere compositions, presence or absence of oxidizing minerals and catalysts, vapor adsorption, and optical pyrolysis correction methods. Watson *et al.* (2005) reviewed different methods and concluded that different studies give different results for method comparisons, and that the citation of a single comparison study is

insufficient to establish comparability. More systematic comparisons are needed that hold most variables constant while varying only a few. In this study, one of the most common methods was used. The OC, EC and carbonate carbon (CO_3^{2-}) fractions were determined from quartz filter samples with a thermal-optical method using a carbon analyzer constructed by Sunset Laboratories. The analyses were performed according to the National Institute for Occupational Safety and Health (NIOSH) method 5040 (NIOSH, 1999). The OC was measured in a helium atmosphere at 300 (OC_1), 470 (OC_2), 610 (OC_3), 865 (OC_4) °C, and the EC in a 2% oxygen 98% helium atmosphere in 550, 620, 700, 780, 850 and 865 °C. Correction of pyrolytic conversion of OC to EC (Pyrol C) was done by laser transmission measurement. Correction of the gaseous phase organics absorbed in the filter material was performed by analyzing the OC content in the back-up filter, and subtracting this amount from that of the front filter OC (Figure 2, **Paper III**). The CO_3 content of the samples was determined indirectly by performing two runs of each filter sample and exposing the second sample punch to HCl vapor, which is presumed to break down the carbonates and, consequently, release the carbonate carbon as CO_2. Thus, the difference between total carbon results gives an estimate of the carbonate carbon content in the sample (Sippula *et al.*, 2007a).

Conversion of the organic carbon (OC) to total organic matter (OM) requires a conversion of the mass of the organic carbon to the total mass of the organic compound using a factor that accounts for the oxygen, hydrogen, and some other elements present. This scale factor ranges between 1.2 and 1.4 for typical atmospheric samples (Gray *et al.*, 1986) and up to 2.0 for wood combustion samples (Turpin and Lim, 2001). In this study, a scale factor of 1.8 was used.

The elemental analyses (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Se, Sr, Th, Ti, Tl, U, V, Zn) were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, hydrogen fluoride nitric acid dissolution), and anions (Br^-, Cl^-, F^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) were performed by ion chromatography (IC) (water elution).

5.5 Analysis of particle morphology

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) are very powerful tools to study the shape and morphology of particles. Equipped with energy dispersive spectroscopy (EDS), they also provide information about elemental composition. While TEM allow a higher resolution down to an atomic scale, SEM usually has a better contrast and leaves more freedom to choose the sampling substrate (Burtscher, 2001). Usually very thin, often copper grids, coated with a carbon film, are used for TEM sampling. The quality of this film and the sampling time play an important role in obtaining a good resolution. If samples are used for quantitative analysis of the size distribution, for example, care has to be taken to have a well-defined size dependence of the sampling process. Both electric field and suction sampling are used. The particles in the grid surface may coagulate during sampling with an electric field, whereas a suction sampler collects single particles.

In this study, particle samples for electron microscopy were collected in the stack on holey carbon copper grids using suction sampling. The samples were analysed by a scanning electron microscope (Leo DSM 982 Gemini) and a transmission electron microscope (Philips CM-200 FEG/STEM operated at 200 kV), including elemental analyses of the single particles from TEM samples by EDS.

5.6 Gas measurements

Single gas analyzers are generally used in combustion experiments and are also suitable for RWC measurements. In the laboratory measurements the sample for the gas analyzers was taken straight from the stack through an insulated and externally heated (180 °C) sample line. Particles were removed from the sample air by a ceramic filter unit. In the laboratory measurements the gaseous compounds were measured continuously with an analyzing rack (ABB Cemas Gas Analyzing Rack) for CO, CO_2,

NO_x and O_2. The organic gaseous substances (OGC, shown as organically bound compounds) were analyzed with a flame ionization detector. The analyzer was calibrated against propane (C_3H_8). In addition, in the field and laboratory measurements the gaseous compounds (NO_x, CO, CO_2, H_2O, SO_2, HCl and 28 calibrated volatile organic compounds) were measured continuously with a Fourier Transform Infrared (FTIR, Gasmet Technologies Ltd.) analyzer. The oxygen concentration was measured with a separate CrO-cell integrated into the FTIR analyzer.

Table 1. The combustion appliances, fuels, test variables and measurements used in the experiments.

Used in publication	**I**	**II**	**III**	**IV**
Test place	laboratory	laboratory	field	laboratory
Combustion appliances	MMH; CMH; SS	CMH	MMH; CMH; S; BO; SS	pellet burner
Fuel	birch wood logs	birch wood logs	mainly birch wood logs	wood pellet; oat; rape; mixed fuels
Test variables	combustion appliances; batch and log size; combustion phases	operational practice: normal and smouldering combustion (batch and log size and restricted combustion air)	habitual use of appliances	fuel; nominal and partial load
Other	combustion process in batch combustion	particle formation	field measurement technique	combustion process in continuous combustion
Dilution	DT; EDs DR = 50:1–300:1	DT DR = 180:1–330:1	PRD+ED DR = 28:1–72:1	PRD+ED DR = 39:1–75:1
Particle mass analysis	PM_1, teflon	PM_1, teflon; DLPI	PM_1, teflon	PM_1, teflon; DLPI
Particle number and size analysis	ELPI	ELPI; FMPS	ELPI: FMPS	ELPI; FMPS
Carbon analysis	thermal-optical	-	thermal-optical	thermal-optical
Ion analysis	IC	-	IC	IC
Metal analysis	ICP-MS	-	ICP-MS	ICP-MS
Morphology analysis	-	Suction sampling, SEM; TEM	-	-
Gas analysis	O_2; CO_2; CO; NO_x; OGC	O_2; CO_2; CO; NO_x; OGC	O_2; CO_2; CO; NO_x; SO_2; HCl; VOCs (FTIR)	O_2; CO_2; CO; NO_x; SO_2; HCl; VOCs (FTIR)
Other analysis	-	-	PAH	-

6 Results and discussion

6.1 Fine particle and gas emissions from RWC

Detailed emission factors from literature and this study are shown in Table 1–3 in Appendix I.

6.1.1 Particle number emissions and number size distributions

Number emission results from RWC are scarce and two primary methods have been used in measurements. Mobility Particle Sizers (FMPS, SMPS and DMPS) measure the number size distributions based on particle electrical mobility, whereas the ELPI classifies particles according to their aerodynamic diameter. Results from these measurements are shown in Table 1 in Appendix I. No significant and systematic difference between electrical mobility and aerodynamic number emission results were observed. Generally, the particle number emissions from RWC appliances were high. On average, there were no clear differences in number emissions between different appliances either. The particle number emission measured by the ELPI from wood pellets varied from 1.0×10^{14} g kg^{-1} to 8.1×10^{14} g kg^{-1}, whereas emissions from the MMH varied between $1.3–5.9 \times 10^{14}$ kg^{-1} and from metal stove and CMH between $2.8–7.0 \times 10^{14}$ kg^{-1} in laboratory measurements (Appendix I, Table 1; **Paper I–IV**). In field measurements, the number emissions were higher, 8×10^{14} kg^{-1} from MMH (**Paper III**) and $24–42 \times 10^{14}$ kg^{-1} from CMHs (**Paper III**), the same as in laboratory measurements.

The particle number emissions did not correspond with the completion of combustion. In the temporary incomplete combustion conditions, e.g. during intermittent operation of the pellet burner or in the firing phase of the masonry heaters, the number emissions increased. However, it was more common in heavily incomplete combustion conditions that, the particle number emission was lower as compared to normal combustion (see Figures 3–5). The particle number emission was related to the particle size in that incomplete combustion produced lower particle number emissions but larger particle sizes than did more complete combustion (**Paper I**; **II;** Figures 3 and 4). In addition, the particle number emission typically increased from batch to batch despite the better combustion conditions with a higher combustion temperature at the end of batch combustion (**Paper I**; Figures 3 and 5).

Generally, the particle number size distributions were dominated by submicron particles, and were temporarily unimodals (Figure 6, **Paper I**; Figure 8, **Paper II**). The particles were very small, and the maxima of the number size distributions varied typically between 40 and 200 nm (**Papers I–IV**). In continuous combustion, the number size distribution was fairly constant. From wood pellet combustion in the pellet burner, for example, the geometric mean diameter (GMD) was on average 52 nm when measured by the FMPS, and it varied by only 2–4 nm (standard deviation) during combustion (Figure 4, **Paper IV**). In batch combustion, the particle number distributions varied between different combustion conditions during the different combustion phases (Figures 3–5). The size distributions were widest during the firing phase, when the sizes of the particles were also larger (**Paper I**;**II)**.

In **Paper I**, the largest GMDs were observed in the operation of the SS and the CMH appliances, where pyrolysis was very fast, whereas the smallest were observed in the operation of the MMH, where pyrolysis was more controlled. In normal combustion in the CMH in the laboratory experiments, the mean GMD was 56 nm (FMPS), whereas it was clearly higher in heavily incomplete combustion, on average 118 nm (Figure 7, **Paper II**).

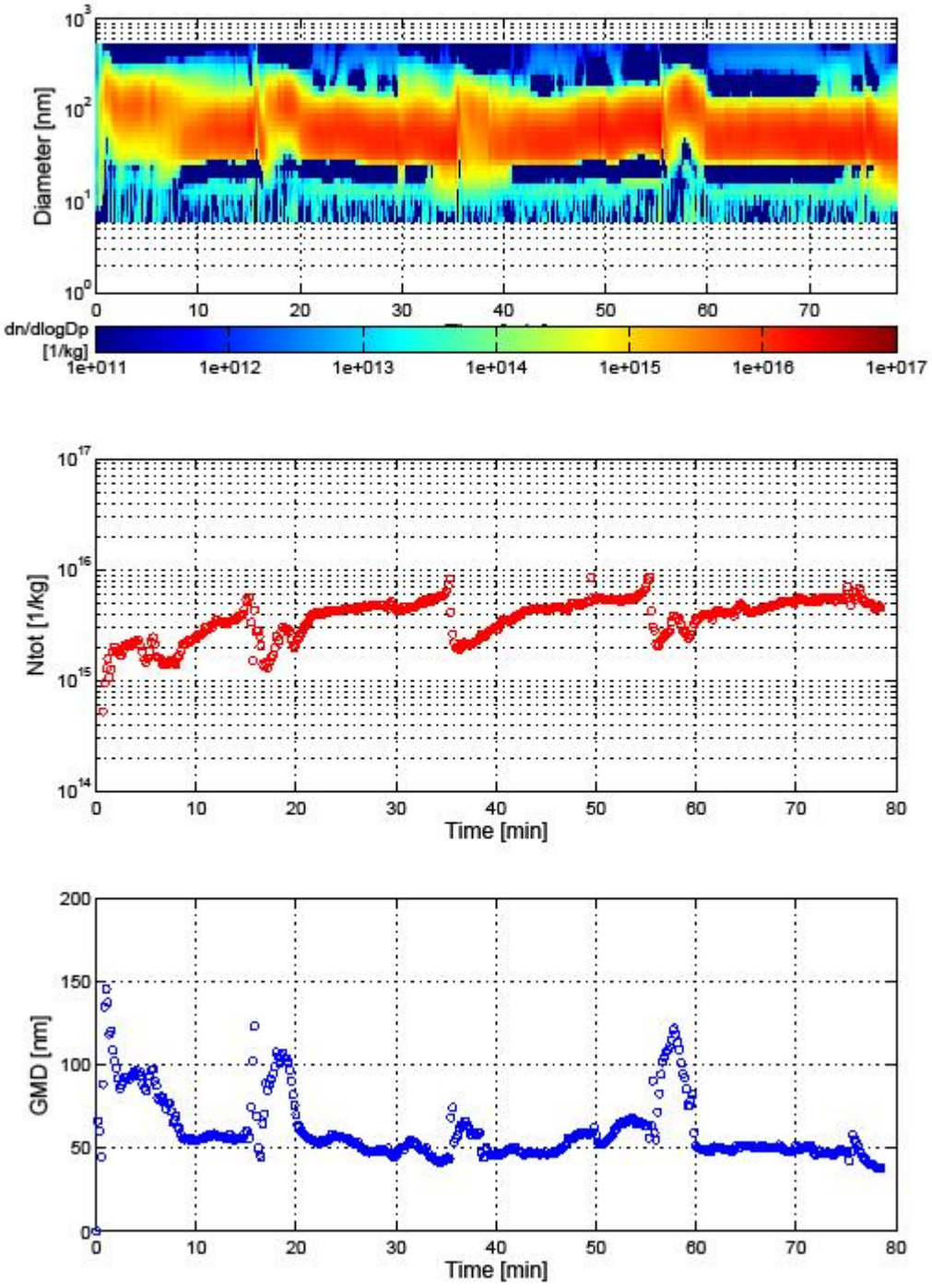


Figure 3. The particle number size distributions, total number emission (N_{tot}) and particle geometric mean size (GMD) as a function of time from the **normal combustion** in the CMH (**Paper II**).

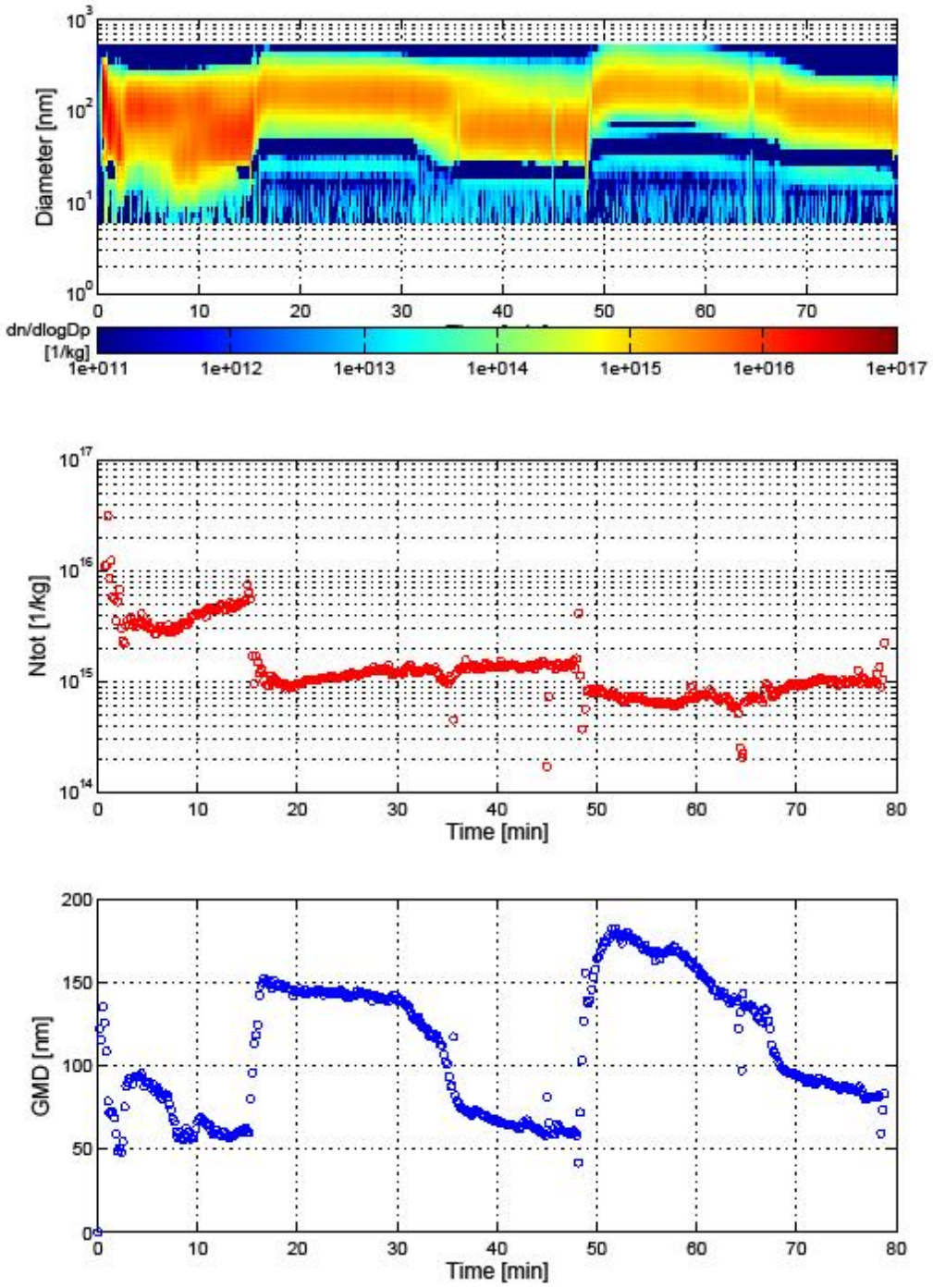


Figure 4. The particle number size distributions, total number emission (N_{tot}) and particle geometric mean size (GMD) as a function of time from the **smouldering combustion** in the CMH (**Paper II**).

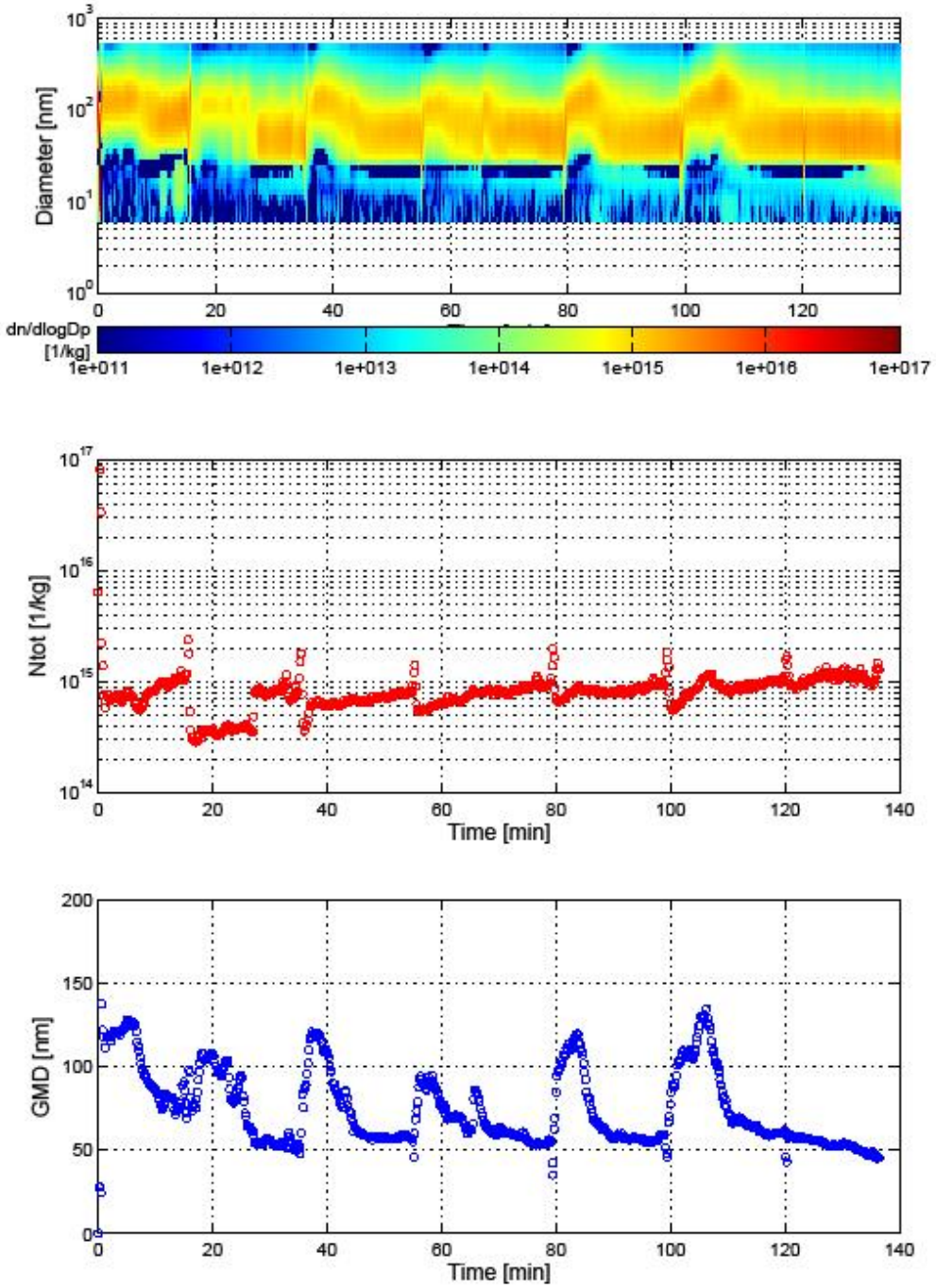


Figure 5. The particle number size distributions, total number emission (N_{tot}) and particle geometric mean size (GMD) as a function of time from the MMH in the field experiments (**Paper III**).

The GMD measured by the FMPS as a function of GMD measured by the ELPI is shown in Figure 7. Generally, the GMDs were slightly larger when measured using the ELPI than when using the FMPS, indicating that particle effective densities were typically above 1 g cm^{-3}. In both devices, the GMD of particles increased when the combustion become more incomplete. The GMD from the FMPS varied from about 40 to 150 nm, whereas the GMD from the ELPI with sintered impaction stages varied from about 50 up to 200 nm. The particle sizes were at the same level as in some other comparable studies (e.g. Hedberg *et al.*, 2002; Hueglin *et al.*, 1997; Gaegauf *et al.*, 2001; Wierzbicka *et al.*, 2005). Hueglin *et al.* (1997) and Gaegauf *et al.* (2001) measured particle sizes from 69 to 96 nm and at around 80 nm, respectively, from wood pellet combustion by SMPS. The GMD measured by the SMPS from a 1 MW grate boiler with pellet combustion was 79 nm (Wierzbicka *et al.*, 2005).

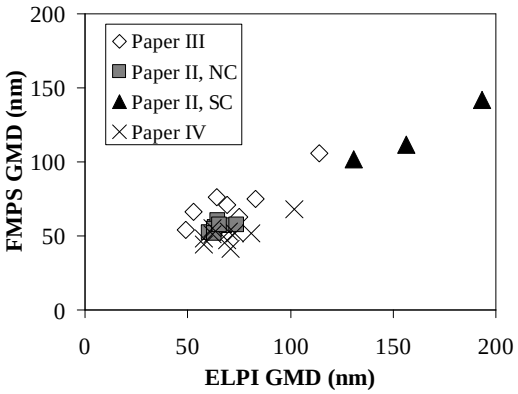


Figure 6. Particle geometric mean size (GMD) measured by the FMPS as a function of GMD measured by the ELPI (sintered stages).

6.1.2 PM_1 emissions and particle mass size distributions

The PM_1 emissions from wood pellet combustion were 0.28 g kg^{-1} (**Paper IV**). The PM_1 emission from the MMH was slightly higher than from pellet appliances, mainly below 1 g kg^{-1}. From the CMH, PM_1 emissions varied from 0.6 to 3.3 g kg^{-1} (Figure 7; Appendix I, Table 2; **Papers II; III**). The PM_1 emissions from the SS were clearly higher, 2.7–5.0 g kg^{-1}, than from other appliances (**Papers I**; **III**). The PM_1 from smouldering combustion in the CMH was the highest, about 10 g kg^{-1} (**Paper II**).

In **Paper I**, the PM_1 emissions during different combustion phases and batches were measured. The contribution of the firing phase was the highest from the CMH, 48% of the total batch PM_1 (0.65 g kg^{-1}) in the first batch, increasing to as much as 86% (1.90 g kg^{-1}) in the last batch. In addition, the PM_1 emission in the last batch was 4.5 times larger than in the first batch, due mainly to the high particle emission during the firing phases (**Paper I**). In the CMHs combustion is more intensive in a hot firebox, but it also accelerates the gasification of the fuel and increases emissions from the batches after the first batch. At the highest gasification rates, the supply of air is not adequate, causing incomplete combustion and high PM_1 emissions.

The PM_1 emissions from pellet combustion were at similar levels as those reported recently by Boman *et al.* (2005) from a pellet stove, and PM by Johansson *et al.* (2004) from pellet burners and boilers. The PM_1 emissions from stoves (e.g. McDonald *et al.*, 2000: 2.3–7.2 g kg^{-1}; Hays et al., 2003: 2.3–10.2 g kg^{-1}) and cookstoves (Venkataraman and Uma Maheswara Rao, 2001: 0.9–2.8 g kg^{-1}) and the PM from fireplaces (e.g. Purvis *et al.*, 2000: 3.3–14.9 g kg^{-1}) were slightly higher or the same level as PM_1 emission from the CMH and SS.

When comparing particle emission factors, the sampling, dilution and measurement techniques need to be considered. Particle losses and particle transformation are the most important factors that affect particle emission factors (see Chapter 6.3). The measurement device used may also have an effect on fine particle emissions. The PM_1 emissions determined from DLPI results were 0–25% lower than the PM_1 determined from filter sampling, probably due to higher particle losses in the cascade impactor as in filter sampling.

The mass size distribution was determined in a few cases. Over 80% of PM_{10} particles were below 1 µm in aerodynamic size (**Paper II**). The

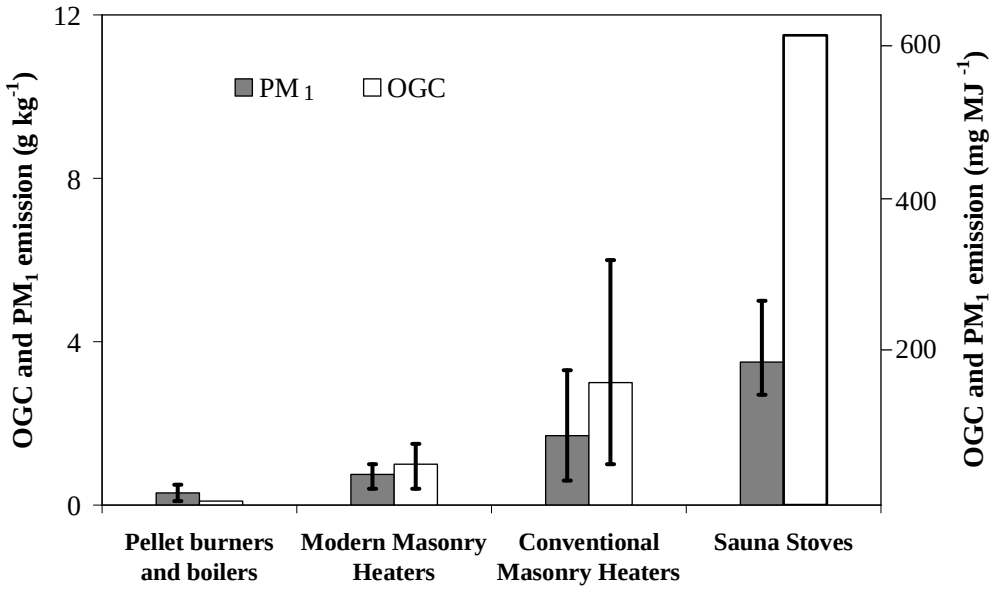


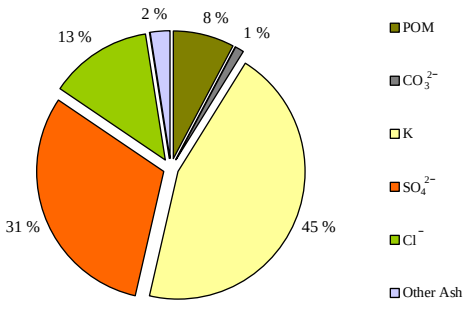
Figure 7. Typical OGC and fine particle mass (PM_1) emission factors and range of factors from Finnish combustion appliances. The figure shows data from Appendix I. Error bars indicate the range of measured values during typical combustion process (not e.g. smouldering combustion).

mass size distributions peaked in one to three modes (**Paper II**). In the submicron range, the mass size distribution was uni- or bimodal depending on combustion conditions. In some cases, there was also an indication of a supermicron mode at around 1–5 µm particle diameter. This coarse particle mode is typically composed of low volatile ash compounds and it is partially unburnt char (Wiinikka, 2005). The MMD measured by the DLPI was 164 nm from wood pellet combustion (Figure 5, **Paper IV**). From the CMH, the MMD was 243 nm in normal combustion and clearly higher, 534 nm, in smouldering combustion (Figure 8, **Paper II**).

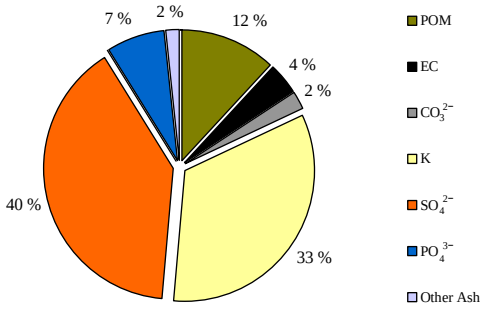
In the study of Boman *et al.* (2005) with a pellet stove, the MMD of the fine mode varied in the range of 117–146 nm. The MMD was higher in three pellet burners (10–15 kW), varying from 200–370 nm measured by the DLPI from pelletized, fresh and stored sawdust (Boman *et al.*, 2004). These burners also had higher CO and PM emissions than the pellet appliances usually do. Kleeman *et al.* (1999) using a MOUDI-impactor found that the particle mass size distributions from wood smoke from a residential fireplace had a single mode that peaks at approximately 100–200 nm particle diameter.

6.1.3 Particle composition

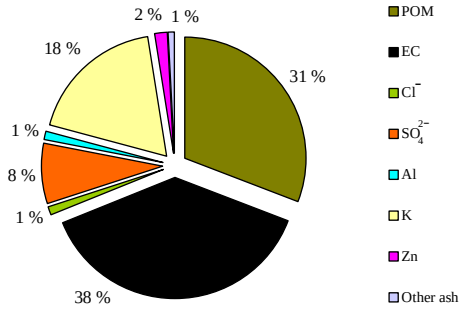
The combustion conditions had clear effects on PM_1 emissions and particle number and mass size distributions. In addition, the chemical composition of the fine particles during RWC was closely dependent on the combustion conditions. From wood pellet combustion, over 90% of the analyzed PM_1 consisted of fine ash compounds (Figure 8). From RWC, this fine ash is composed mainly of potassium compounds (see Chapter 3.3). The phosphate containing compounds were an important species in the fine particles emitted from agricultural fuel combustion, in contrast to wood fuels (**Paper IV**; Figure 8). From the pellet burner, the amounts of incomplete combustion products, EC and POM, were low, typically below 10% (Figure 8). These results are well comparable with previous studies of wood pellet combustion (Sippula *et al.*, 2007a,b), but slightly higher EC and POM



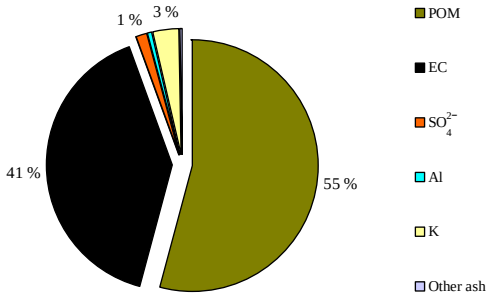
Pellet burner
wood pellets (PM_1 0.26 g kg^{-1})



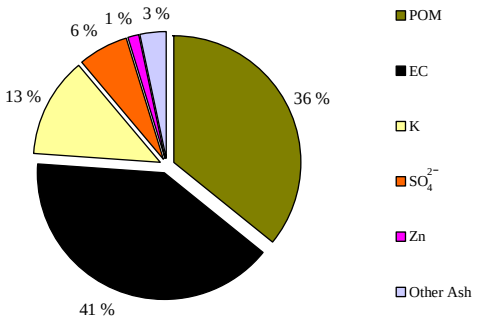
Pellet burner
rape seeds (PM_1 0.30 g kg^{-1})



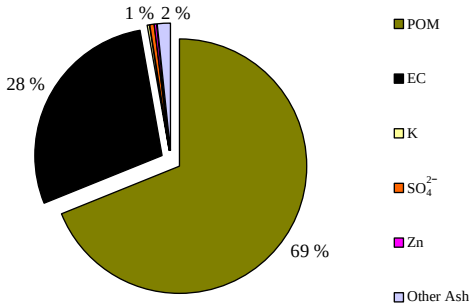
MMH (field, PM_1 0.8 g kg^{-1})



SS (field, PM_1 4.3 g kg^{-1})



CMH NC (PM_1 2.3 g kg^{-1})



CMH SC (PM_1 7.3 g kg^{-1})

Figure 8. Typical chemical compositions of PM_1 samples (in mass-%) from RWC appliances (**Papers III–IV**; normal (NC) and smouldering (SC) combustion calculated from the Frey *et al.*, 2008).

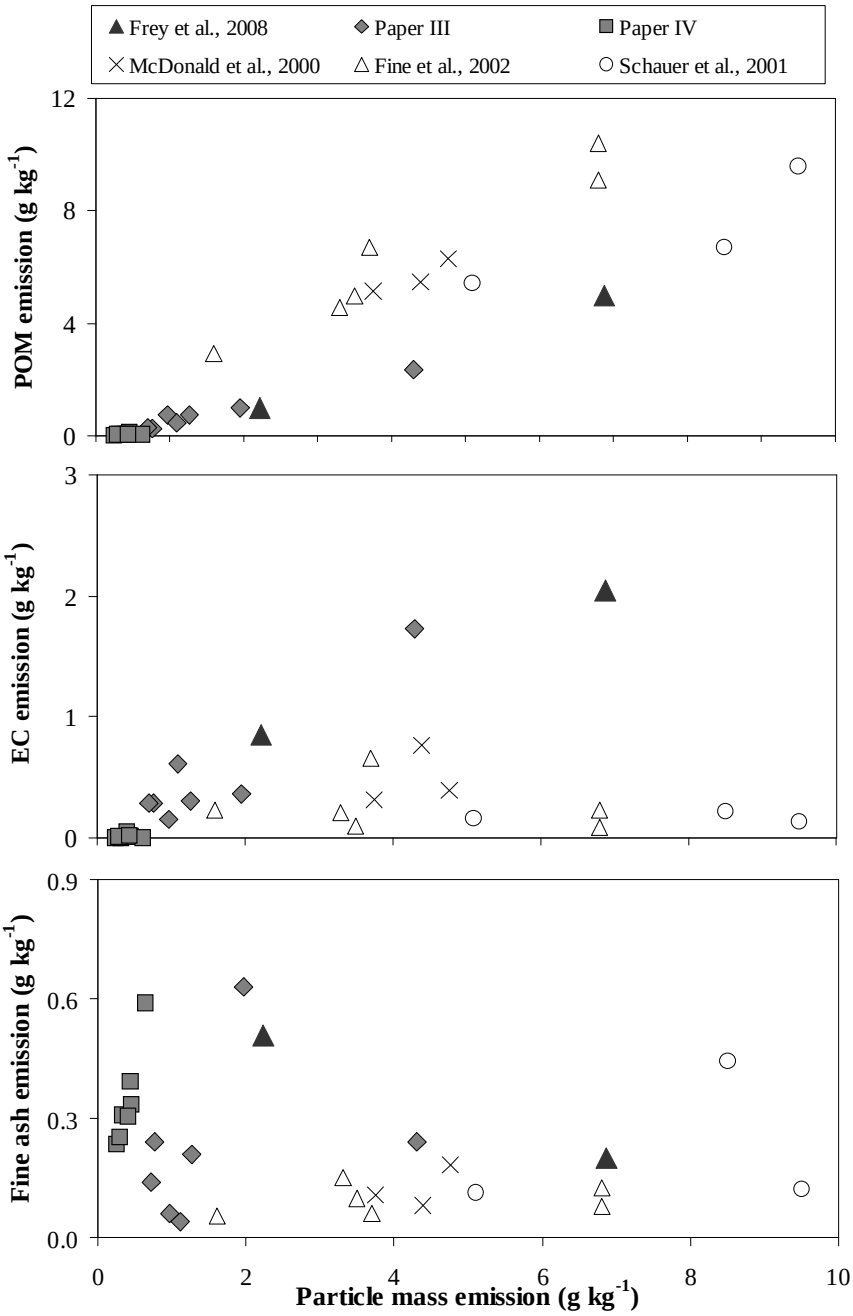


Figure 9. POM, EC and fine ash emissions as a function of particle mass emission measured from diluted flue gas. OC is normalized to POM by multiplying by a factor of 1.8. In this study (grey points) the particle mass is PM_1 (normal and smouldering combustion values calculated from the Frey *et al.*, 2008), and in the studies by Schauer *et al.* (2002) and Fine *et al.* (2001) the particle mass is $PM_{2.5}$.

contents have also been measured. Wierzbicka *et al.* (2005) found that the OC fraction from the combustion of 1–5 MW pellet boilers at medium load varied from 9 to 14% and the EC varied from 18 to 56% of PM_1.

From masonry heaters, the fine ash emissions were at a similar level as from pellet combustion, but the amount of incomplete combustion products, EC and POM, were considerably higher, since 20–30% of PM_1 was ash. In addition, EC emission was higher than POM emission. In the field measurements, the composition of PM_1 from the MMH was almost the same as from the CMH in laboratory measurements (Figure 8). However, in separately performed tests on the MMH we observed that as much as 50% of the PM_1 sample was made up of ash compounds, and that it contained only small amounts of organics (below 20%). From the sauna stove, the analyzed PM_1 was composed mainly of EC (55%) and POM (41%) (Figure 8). From slow heating combustion, the percentage of POM even increased: it was 69% of analyzed PM_1 in smouldering combustion in **Paper II** (Figure 8).

In most previous studies, the fine particles emitted from batch-fired appliances have been composed mainly of organic material and EC, while the ash content has been relatively low. For example, Fine *et al.* (2001) reported that from 40% to almost 100% of fine particle mass was organic material in the case of a conventional fireplace. The fractions of EC in fine particles have been reported to vary from 1–31 % (Fine *et al.*, 2001; Schauer *et al.*, 2001). In a study quantifying 350 chemical compounds from wood combustion, the fraction of POM (OC normalized by multiplying by 1.2 to compensate for oxy species in POM) was more than 80%, the fraction of EC was below 20% and the fraction of analyzed ash compounds were below 4% from the combustion of soft and hard woods in fireplaces and wood stoves (McDonald *et al.*, 2000). Schauer *et al.* (2001) found that the ash fraction was about 1–5% from the combustion of pine, oak and eucalyptus in a fireplace. Thus, it seems that the proportion of soot and particularly fine ash in PM_1 is clearly higher from masonry heaters and sauna stoves than from other batch combustion appliances. In addition, the high fraction of POM seems to represent heavily incomplete combustion.

Figure 9 summarizes the particle composition results from **Papers II–IV** and from some recent studies. In these **Papers**, the POM (R^2 = 0.97) and EC (R^2 = 0.93) correlated very well with analyzed PM_1 emissions. When the PM_1 emission factor is higher than 0.4 g kg^{-1}, the combustion conditions become more incomplete and both EC and POM increased remarkably, POM emission more strongly (slope 0.71) than EC (slope 0.34). Other studies also report quite good correlation between particle mass and POM. The POM emission in the studies of McDonald *et al.* (2000) and Fine *et al.* (2001) increased faster than in the studies reported in **Papers II–IV**, when a similar OC normalization (1.8) was used (Figure 9). The composition of the organic fraction of PM emissions may be different in the birch wood combustion in this study and the pine, oak, eucalyptus, poplar, hickory etc. combustion, and probably a different OC normalization should to be used. On the other hand, the EC emission did not at all correlate with the PM in the studies of Fine *et al.* (2001) and Schauer *et al.* (2002) (Figure 9). However, the EC (i.e. soot) is a tracer of incomplete combustion (see Chapter 3.2) and the EC emission should correspond with the incompleteness of combustion. One of the most important factor that affect the emission factor of EC is the method and protocol used in the EC analysis. In particular, the methods used for pyrolysis corrections have significant effects on both OC and EC results, which probably also explains the differences in the POM results between this study and other studies.

The fine ash emission had no significant correlation with the PM emissions (Figure 9). The vaporization of alkali metals is dependent on the chemical composition of the wood and the reactions of inorganic species (e.g. Sippula *et al.*, 2007a). The combustion temperature also has an important influence on vaporization, so that greater amounts of ash particles are released at high than at low temperatures (Davidsson *et al.*, 2002; Knudsen *et al.*, 2004). Since the chemical composition of ash does not vary between

different pure wood fuels, it seems that the combustion temperature is the primary factor that affects the fine ash emission in RWC. For example, in **Paper II**, the low combustion temperature in smouldering combustion produced low ash emissions, whereas high temperatures produced high emissions (Figure 9). In addition, the amount of ash species increased from batch to batch due to the increase in the combustion temperature in subsequent batches (**Paper I**). In **Paper I**, similar PM_1 emissions from the CMH and the MMH can be explained by the higher release of alkali metal particles with the higher combustion temperature from combustion in the MMH (**Paper I**).

Sippula *et al.* (2007) found that the higher ash content of the bark fuels in the pellet stove increased both the fly ash emission and the products of incomplete combustion. In addition, it was observed in **Paper IV** that although the fuel ash content of the other agricultural fuels were considerably higher than that of wood fuel, the PM_1 emission from rape seeds, for example, was surprisingly at the same level as that from wood pellets. Thus, the chemical composition of the fuel ash had a strong effect on the release of alkali metals. It seems that one important factor explaining the observed differences in the release of ash-forming elements is the formation of alkali metal chlorides, which is seen in the clear correlation between the release of chlorine and of ash in the fine particles (**Paper IV**).

6.1.4 Particle morphology

The study of particle morphology is particularly important because it provides knowledge of the composition, size and shape of the primary particles. However, information on fine particle morphology in RWC is very scarce.

In this study, detailed information on fine particle morphology during different combustion conditions from CMH was obtained. In SEM and TEM analyses, both large agglomerates (**Paper II**: Fig. 9d–f, Fig.11) and separate spherical and irregularly shaped particles were observed (**Paper II**: Fig. 9d–f, Fig. 13, Fig. 14). Large agglomerates were found to contain mainly carbon and are considered to be primarily soot particles. The fine ash particles seemed to occur mainly as separate spherical or irregularly shaped particles but not as agglomerates. The separate ultrafine particles were composed mainly of K, S and Zn, but also in a lesser extent of C, Ca, Fe, Mg, Cl, P and Na (**Paper II**: Fig. 12). The larger spherical and irregularly shaped particles were composed of same alkali metal compounds, but they were probably covered with heavy organic compounds. Separate particles were to some extent connected with agglomerates. From the smouldering combustion conditions, the surfaces of particles were covered by organic species and the particles had a more closed (sintered-like) structure than the particles from normal combustion (**Paper II**: Fig. 14). In the separately performed experiments (unpublished results), it was observed that the fine particles included a number of irregular, e.g. tube-shaped particles, which are doubtless residual fly ash particles ejected from the grate and carried to the flue gas.

Agglomerate-like particles have been common also in other wood combustion studies (e.g. Colbeck *et al.*, 1997; Kocbach *et al.*, 2005; Sippula *et al.*, 2007a). Kochbach *et al.* (2005) found that while agglomerates from vehicle exhaust were characterised by high levels of Si and Ca, agglomerates from wood smoke were characterised by high levels of K. Kochbach *et al.* (2005) have also reported that the size of primary particles of agglomerates was similar to that found in this study, 37–39 nm (±11 nm). Sippula *et al.* (2007a) observed that most of the particles from a pellet stove observed by SEM were single almost spherical primary (ash) particles, and only a few larger agglomerate particles were present in the samples. Kochbach *et al.* (2005) also found large spherical particles that were carbon dominated from the low-temperature combustion of wood.

In summary, it seems that the morphology of RWC particles is complex and varies between different combustion conditions. According to parallel particle size distribution and morphology measurements in this study, it seems that the released ash particles may play an important role in the formation of the particle number emission in RWC. In the present experiments, the ultrafine mode in the particle number distributions seemed

to be determined mainly by the amount of released ash forming material in combustion. Respectively, the shifting of particle size during different combustion conditions seemed to be determined by the amount of condensed organic vapour in the flue gas (**Paper II**).

6.1.5 Gas emission

The CO and OGC are gas emissions that indicate the incompleteness of secondary combustion. The CO and OGC emission factors are shown in Figures 7 and 10. These emissions were low in continuous combustion. In **Paper IV**, the CO emission from the combustion of wood pellets in a pellet burner was 0.55 g kg^{-1}. The CO emissions from agricultural fuels was about 3-fold those from wood pellet. Wood chips combustion seemed to increase slightly the CO emissions when compared with pellet combustion (Appendix I, Table 3).

The CO emission from pellet combustion was slightly lower than in the study of Johansson *et al.* (2004) (0.6–2.3 g kg^{-1}; Appendix I, Table 3). The OGC emissions are typically low from continuous combustion, primarily below 0.1 g kg^{-1} (Launhardt and Thoma, 2000; Johansson *et al.*, 2004; Appendix I, Table 3).

The CO and OGC emissions were clearly higher from batch combustion appliances than from continuous combustion appliances. The lowest gas emissions were measured from MMHs, in which the CO emission was 14 g kg^{-1} and OGC 0.4 gC kg^{-1} in the laboratory (**Paper I**), and CO 28 g kg^{-1} in the field experiments (**Paper III**). The CO from the CMHs varied from 22 to 68 g kg^{-1} and OGC 1.9 to 6 gC kg^{-1} (**Papers I–III**). The CO emission values from the CMH (**Papers I–III**) are well comparable with those reported in other studies of stoves or fireplaces (e.g. EPA, 1996a; Venkataraman and Uma Maheswara Rao, 2001; Koyuncu and Pinar, 2007), whereas OGC emissions were lower than in other studies (e.g. Bhattacharya *et al.*, 2002; Hübner *et al.*, 2005). Conversely, CO and OGC emissions from the SS are mainly higher than from other appliances. In **Paper I**, the OGC and CO emissions from the SS were about 24-fold and 4-fold higher, respectively, than from the MMH. Extremely high emissions, CO up to 300 g kg^{-1} and OGC up to 90 gC kg^{-1}, have been measured from old-type wood log boilers with big batch size (Johansson *et al.*, 2004). The smouldering combustion from the CMH produced emission factors of 150 g kg^{-1} CO and 30 gC kg^{-1} OGC (**Paper II**).

From the masonry heaters and sauna stoves, large variations (10 to 100 times) in gas emission factors were observed from the firing to burn out phases (**Paper I**). The highest emissions were caused by the high gasification rate during the firing phase that led to an insufficient supply of air and insufficient mixing of air and fuel. The OGC and CO emissions were concentrated on the firing phase and decreased rapidly with time afterwards (Figure 3, **Paper I**). However, CO emissions were also high during the burn out phases. This is due to the low diffusion rate of oxygen to the char and the cooling of the combustion chamber due to the high volume of excess air in the combustion chamber. In most cases the combustion temperature decreased below 800 °C, which is the level needed for complete oxidation of CO (Nussbaumer, 2003; Van Loo and Koppejan, 2008).

Regarding other gas emissions, the NOx levels were relatively low and were similar in all measurements for wood fuels (**Paper III**; **IV**), since at low temperatures NO_x emissions arise only from fuel nitrogen. However, the emissions of NO_x, SO_2 and HCl from combustion of agricultural fuels were from 4- to 148-fold those of wood fuel due to the higher N, S and Cl content in agricultural fuels (**Paper IV**).

6.2 Effect of operational practices on emissions

6.2.1 Effect of operation in continuous combustion

Emissions in continuous combustion appliances were typically low, but increased at partial or low loads, in the on-off use and cleaning periods. In these cases the emissions of PM_1, EC and POM increased, indicating more incomplete combustion conditions at partial than at nominal load (**Paper IV**). Typically, particle

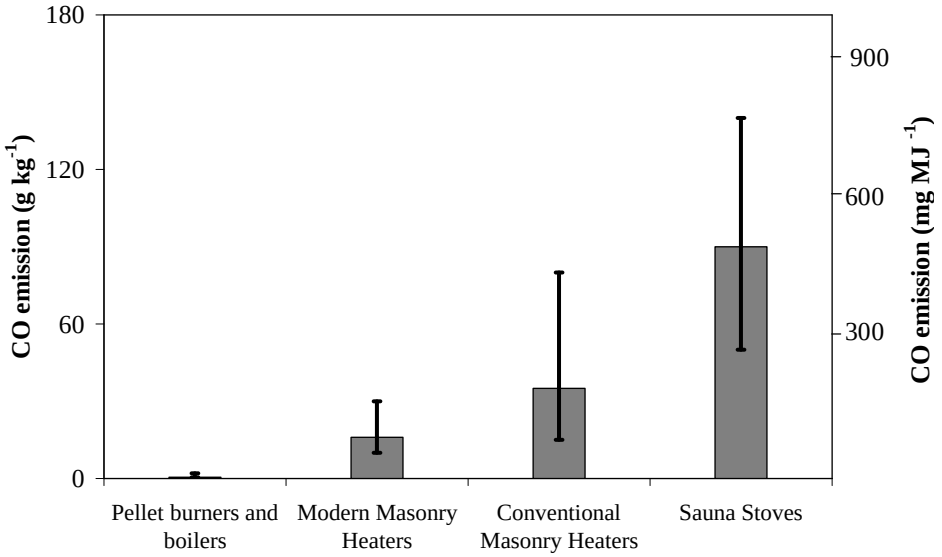


Figure 10. Typical CO emission factors and range of factors from Finnish combustion appliances. The figure shows data from Appendix I. Error bars indicate the range of measured values during typical combustion process (not e.g. smouldering combustion).

size increased during such operation (**Paper IV**). The effects of burner type (e.g. top-, under- or side-feed) on emissions have not been widely studied, but studies of top-feed pellet stoves and under-feed pellet burners have not found significant differences in particle number size distributions (Tissari *et al.,* 2004a). Operation at partial load, when the combustion process is continuous, has been observed to increase emissions only slightly (Johansson *et al.,* 2004). A very low load leads to the intermittent operation of burners, which has a significant effect on particle and gaseous emissions, and it is dependent on operation type of burner (Johansson *et al.,* 2004). With electrical ignition in the burner, the emissions were only slightly higher in intermitent than continuous operation, because the ignition and burn-out phases take very little time (**Paper IV**). With the pilot flame, Johansson *et al.* (2004) found 3-, 27-, 63-fold emissions of PM, CO and OGC, respectively.

Some of the pellet burners have a cleaning operation as a result of which particle and CO emissions increase sharply for a short period (Tissari *et al.,* 2004a). Typically, the cleaning periods increase the combustion air flow through the grate and decrease the fuel supply momentarily what cleans the grate holes (Sippula *et al.,* 2007a). For particle emissions, the contribution of the cleaning periods to the whole emission was less than 10%, but they contributed up to 30% of the whole CO emissions.

6.2.2 Effect of fuel loading on emissions in batch combustion

Fuel loading had a clear influence on emissions. The use of too large fuel batches or small logs (i.e. total area of wood logs) in relation to the size of the heater air intakes causes incomplete combustion. With a large batch size (dry fuel), the gasification rate of the fuel increases and the supply of air becomes insufficient (**Paper I**). When the batch size was doubled, all emissions from the CMH increased, except the particle number emission: the OGC emissions were 4.0, CO 2.2 and PM_1 1.9 times higher (**Paper I**). For up-draught combustion in a wood boiler, Johansson *et al.* (2004) observed that PM emission from a large fuel load was 4 times higher than from a small one. In addition, the use of heat storage decreased CO and OGC

emissions, 15–28% and 40–50 %, respectively, compared with emissions from a small batch (Johansson *et al.,* 2004). The log size affected emissions more than did batch size (**Paper I**). Using equal batch sizes, emissions from small logs were 8.7-fold for OGC, 2.3-fold for CO, 1.4-fold for particle number and 4.8-fold for PM_1 higher than from big logs. Wet fuel restricts the combustion rate of wood. Johansson *et al.* (2004) investigated the emissions from a ceramic wood boiler with a flue gas fan and a down-draught boiler using dry and wet wood log fuels. They found that wood fuel with a moisture content of 26% givea the lowest emissions, whereas the dry fuel produced slightly higher (1–3-fold) and the wet (38%) fuel clearly higher, 7-fold CO, 21-fold OGC and 4-fold PM, emissions. However, it is important to note that this kind of findings are very appliance (case to case) related and the relation between batch size-log size-fuel moisture on the emissions is very complex and may differ between different appliances.

6.2.3 Emissions in smouldering combustion

Smouldering combustion is responsible for a significant number of air quality problems locally and temporarily (Glasius *et al.,* 2006). The most problematic appliances are multi-fuel boilers, which can burn wood, oil, or pellets, but they commonly use wood log combustion with an up-draught technique. In addition, light stoves are typically used with low combustion rates by restricting the air intakes which lead smouldering combustion. Furthermore, too high a burn rate (large fuel batches) causes an insufficient air supply and smouldering-like combustion from masonry heaters and sauna stoves. In **Paper II**, emissions in conditions of heavily incomplete combustion were studied in more detail. In smouldering combustion (SC), where small logs and big batches were used, and the air intakes were closed, the combustion temperature was lower than in normal combustion (NC), and the air supply was clearly inadequate Incomplete secondary combustion of the gaseous organic compounds in SC increased the emission of OGC to 14-fold and POM to 7-fold that in NC. The smallest effects were observed in CO (3.5-fold) and EC emissions (2-fold), which are also products of incomplete combustion. Because the fine particles were composed mainly of organic matter in SC, the PM_1 emission was also clearly higher, about 6-fold that in NC. In contrast, the ash and particle number emissions were less than half those in NC. Furthermore, the particle size in SC was about 2-fold that in NC. In SC, the particles were covered by organic compounds, due to the condensation of organic matter on the surfaces of the agglomerates (see 6.1.4).

Johansson *et al.* (2004) found even higher emissions from the combustion of an old-type wood log boiler with a big batch size. The CO emissions were 300 g kg^{-1}, OGC 90 gC kg^{-1} and PM 42 g kg^{-1}, whereas in **Paper II** they were 150, 30 and about 10 g kg^{-1}, respectively. Jordan and Seen (2005) observed nearly the same PM emission factor as Johansson *et al.* (2004), as much as 40 g kg^{-1} from a wood stove with hood dilution and restricted combustion air (a low burn rate), which is about 4-fold the PM_1 emissions in smouldering combustion in the CMH in **Paper II**.

6.3 Effect of sampling and dilution on fine particle emissions

The measurement methods used can have a strong influence on particle emissions. Organic emissions and particle losses are particularly dependent on the sampling and dilution method. However, there are no general standards or methods to measure fine particles from small combustion devices. In this section, the effects of sampling and dilution on emissions are discussed briefly, concentrating on particle mass.

6.3.1 Particle losses

Particle losses are important when the total PM including coarse (~1–10 µm) and super coarse (>10 µm) particles are measured. PM losses are caused by settling, impaction and other inertial effects and are dependent on particle size (Baron and Willeke, 2001). There were losses of over 50% for 5 µm particles, and no significant losses for particles below 1 µm, in two ejector diluters in series (Wierzbicka *et al.,* 2005). There

are also significant losses of coarse particles in hood dilution systems, which are widely used in RWC measurements (e.g. EPA Method 5G, NS 3058-2 Method in Norway), but not enough attention is paid to them. In such systems, the particle deposition is dependent on the flow rates of the system, and varies between systems.

Several studies show that the PM from RWC is totally dominated by fine particles (e.g. Boman *et al.*, 2005). However, coarse and super coarse particle emissions may play an important role in PM. The occurrence of these particles is sporadic and is dependent on the combustion appliance. Super coarse particles are residual fly ash particles that are ejected from the grate. For example, the operation of a sauna stove with a high combustion rate and short gas ducts leads to enrichment of coarse and super coarse particles in the flue gas. In masonry heaters with very long ducts (cf. Figure 1a and c in **Paper I**), the coarse particle losses in the heaters are high and they not occur in the flue gas. When the air supply through the grate is low in modern masonry heaters or in the slow heating stoves, for example, the emissions of coarse particles are also low.

The measurement of coarse and super coarse particles is very difficult particularly from batch combustion. Isokineticity is not easy to perform due to variable processes and low flow rates in the chimney. Several parallel measurements of diluted PM_1 and total PM from hot flue gas were performed from masonry heaters and sauna stoves (Appendix I, Table 2). According to these unpublished experiments, PM was not mostly dominated by PM_1 and typically only 30–40% of PM was below 1 µm. However, in some cases PM_1 from diluted gas was higher than PM in hot gas. The high fraction of coarse particles is probably due to the high flow rates used in Finnish appliances, which leads to the occurrence of super coarse particles in the chimney.

6.3.2 Transformation of particles

The transformation (nucleation, condensation, coagulation, evaporation) of particles is also important in combustion aerosol sampling (e.g. Turrek, 2004). The methods used have a strong influence on the emission results, particularly on organic emissions (Amann and Siegla, 1982; Hildemann *et al.*, 1989; Lipsky and Robinson, 2006). Emissions of EC do not seem to vary with dilution (Lipsky and Robinson, 2006).

Dilution is critical for particle sizes in the nucleation mode (Turrek, 2004). When dilution air is not heated (i.e. is at ambient temperature) and is not dried, nucleation of volatile organic compounds as well as sulphates and nitrates tend to form new nanoparticles (Shi and Harrison, 1999). Nucleation in the dilution has been observed from diesel engines, for example, when sulphur rich fuel was used (Vaaraslahti *et al.*, 2004).

In this study it was found that organic vapours do not easily form particles by nucleation despite their high concentration in flue gas (**Paper II**), but rather condensate on the surfaces of the existing particles. It also has been reported that hydrocarbons condense onto existing particles rather than form new particles by nucleation (Pyykönen *et al.*, 2007). The large surface area of existing particles (both soot and ash) during the gas-to-particle conversion of organic vapours can also affect this result. However, in **Paper III** it was observed in wintertime field experiments that the nucleation of organic compounds does not occur in the firebox but rather in the chimney when, in addition to smouldering combustion, the prevailing physical conditions in the flue gas are also favourable. The occurrence of very small particle mode (6–30 nm) from RWC is very rare and has not been reported earlier.

In incomplete combustion conditions the gas-to-particle conversion of organic vapours has a significant effect on PM emission. At low levels of dilution, semivolatile species occur mainly in the particle phase, but increasing dilution reduces the concentration of semivolatile species, shifting this material to the gas phase in order to maintain phase equilibrium (Lipsky and Robinson, 2006). For example, a field comparison of a stack sampler with EPA Method 5 has shown that this sampler collects about ten times as much organic material as the hot filter

portion of the Method 5 train (Hildemann *et al.*, 1989). Purvis *et al.* (2000) found in fireplace tests that the temperature at which the particle sample was collected had a major impact on the $PM_{2.5}$/PM fraction when the DR was moved from 4.3 to 11.0 in the hood dilution method. Hedberg *et al.* (2002) observed that the size distributions were not severely affected by the dilution ratios from wood stove measurement. Boman *et al.* (2005) found that the sampling conditions did not influence either the emission of PM or the particle size distribution, but increased concentrations of OGC and PAH were observed when the dilution ratio was increased from 3 to 7. However, in that study the dilution ratios were low and the appliance studied was a pellet stove, which has low organic emissions, so it did not affect the PM. Lipsky and Robinson (2006) concluded in a study measuring the partitioning of semivolatile materials under atmospheric conditions that partitioning theory indicates that dilution samplers need to be operated in such a way that the diluted exhaust achieves atmospheric levels of dilution. They found that too little dilution can overestimate fine particle mass emissions, and too much dilution (with clean air) can underestimate them (Lipsky and Robinson, 2006). In order to get maximum PM, the DR should to be about ten (Amann and Siegla, 1982).

In summary, the measurement methods used have a strong influence on the PM emission results, particularly on organic emissions and the fraction of coarse particles. The results from the relation of PM1/PM are inconsistent due to the coarse particle and POM losses in the sampling and dilution.

6.4 Cases of high and low fine particle emissions from RWC appliances and suggestions for emission reduction measures

Combustion conditions vary significantly between different combustion appliances and operational practices, and this affects emission factors remarkably. The factors that influence fine particle and gas emissions from RWC are summarized in Figure 11. Even a small difference in the combustion conditions increases the emissions, their properties and their effects remarkably. It should also be noticed that the measured emission (physical and chemical composition of particles and gases) does not exactly correlate with the emission into the atmosphere. This also leads to the assumption that the estimated effects of RWC emissions are not the same as the real effects (Figure 11). Because of the large number of uncontrolled factors that affect combustion conditions, the importance of single factors is not easy to determine exactly. According to this study, the most important factors that affect **high** fine particle emissions are:

1) The overall lack of available oxygen (smouldering combustion). The most problematic appliances are multi-fuel boilers (without heat storage tanks), which can burn wood, oil, or pellets, but are primarily used in wood log combustion with an up-draught technique. In addition, because of the lower temporary need for heat, light stoves are typically used with low combustion rates by restricting air intakes, which leads to smouldering combustion. In the worst cases, PM emission factors up to 40 g kg^{-1} are found. For good combustion quality, short charging intervals with small batch size are required. The use of a heat storage tank is advisable for the combustion of wood log boilers.

2) The conventional combustion technique in sauna stoves. Emissions from SSs are high (PM_1 up to 5 g kg^{-1}) because of the conventional combustion technique. SSs have to operate with the high combustion rate because the need for heat in the sauna room is temporarily high. The firebox is small and secondary combustion is not possible, so the efficiency is low. In addition, with high gasification rates the supply of air is clearly insufficient, causing distinctly incomplete combustion in SS operation. To reduce emissions of sauna stoves, the combustion technique must be developed or secondary removal techniques are needed.

3) Too fast pyrolysis and combustion rate in masonry heaters and sauna stoves. The size of the air intakes in Finnish heaters is restricted and the operating temperature in the firebox is high. Thus, the occurrence of a too

high gasification rate is typical due to excessively large fuel batches in relation to the size of the air intakes, which leads to an insufficient supply of air. Thus, controlling the gasification rate via the primary air supply, log and batch size, as well as fuel moisture content, is important for the reduction of emissions in conventional Finnish appliances.

4) Too low combustion temperature. In open fireplaces, cookstoves or camp-fires, much heat is often lost to the surroundings due to the lack of radiative heat, which restricts combustion temperature and increases emissions. The use of wet fuel also decreases the combustion temperature. In the ceramic wood log boiler, wet fuel increased emissions 3–4-fold, from 0.4–0.6 g kg^{-1} to 1.7 g kg^{-1} (Johansson *et al.*, 2004).

5) Operation of burners at low load. Presently, most pellet and stoker burner systems do not have heat storage tanks, and the boiler is set at thermostat control, which results in a cyclic intermittent operation of the burner. Combustion at low loads increases remarkably the emissions from burners that operate with a pilot flame (Johansson *et al.*, 2004: PM_1 increased from 0.4 up to 1.2 g kg^{-1}). In addition, pellet combustion units with pilot flames should be of a size that allows continuous combustion. If this is not possible, these appliances should also be equipped with heat storage tanks.

Emissions in RWC are **low**:

1) In the continuous combustion of pellet or stoker-burners, because the burners have heat control devices and are equipped with effective heat exhangers and advanced control devices such as an O_2-sensor. The fuel is fed according to the heat demand and combusted at a high temperature in a small grate with staged air. Emissions are typically low (PM_1 typically below 0.3 g kg^{-1}) and fine particles are composed mainly of released alkali metal compounds. Thus, the release of alkali metals, which is dependent on fuel ash content, the chemical composition of ash, and the combustion temperature, are the primary factors that determine fine particle emissions from continuous combustion.

2) Emissions of **modern wood log boilers** are also low, PM typically 0.4–0.6 g kg^{-1} due to the fact that they are equipped with a hot firebox insulated with ceramics, advanced control devices such as an O_2-sensor, air control and staged air combustion.

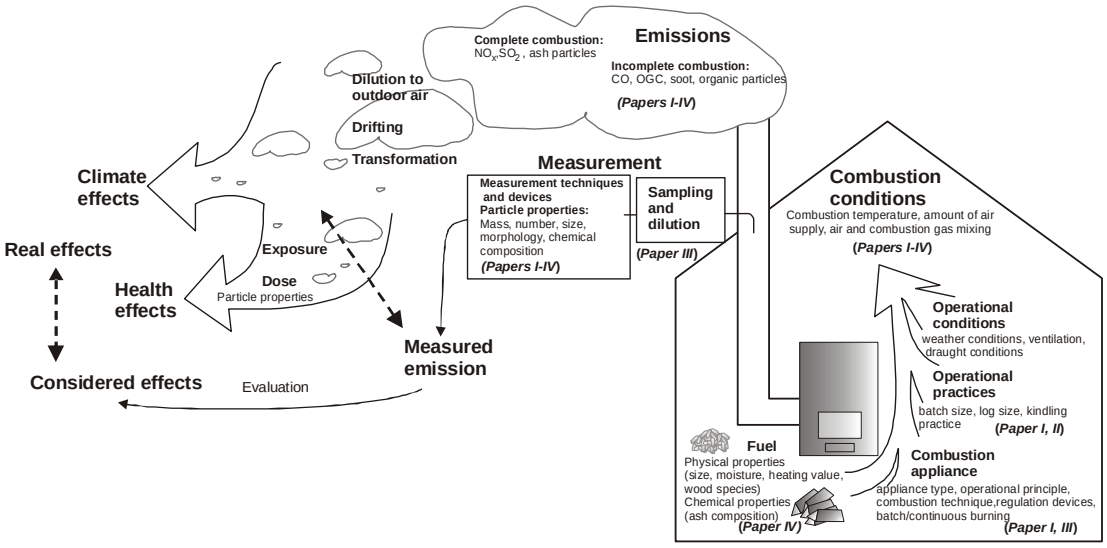


Figure 11. The general picture of the factors influencing fine particle emissions from RWC.

3) In masonry heaters, hot and closed firebox surfaces reflect heat back into the flame and create the gas turbulence needed for complete combustion. In addition, the secondary combustion chamber enhances secondary combustion, and the large mass gives good efficiency. With an optimal operational technique, emissions from CMHs are low. In this study, in the best cases PM_1 was as low as 0.6 g kg^{-1}, whereas typical values are about 1.6–1.8 g kg^{-1}, and the highest values are 3.3 g kg^{-1} with the same appliance.

4) In MODERN masonry heaters, in contrast to CMHs, the primary airflow is controlled and secondary air is distributed to envelop the fuel batch e.g. from the small air inlet holes in the grate. These holes enhance the mixing of air and combustion gases. Preheating of secondary air at the expense of the grate temperature probably decreases the release of alkali metal compounds, but enhances secondary combustion. The decreased air supply through the grate also decreases the flow through the grate and the ejection of coarse particles to the flue gas. The operation at lower overall excess air increases the combustion temperature. Thus, the emissions caused by incomplete combustion during pyrolysis are reduced very efficiently and the composition of the emissions is similar to that of emissions from continuous combustion from a pellet burner, for example. In the best cases, PM_1 emissions were 0.3–0.5 g kg^{-1}, whereas typical values are about 0.7–0.8 g kg^{-1}. The effect of poor operational practice on emissions in MMH has not been studied.

7 Summary and conclusions

Residential wood combustion (RWC) appliances have a high probability of incomplete combustion, producing fine particles and hazardous organic compounds. Generally, there are several studies on emissions from RWC appliances. However, knowledge on the emissions from wood-fired appliances, especially concerning the fine particle emissions and their composition during different combustion conditions has been limited. Moreover, there have not been any scientific studies from emissions in the Finnish context. This information is needed to develop low emission combustion techniques, to better understand the relation between certain health, and climate effects and, to put right efforts and measures to reduce these problems.

In this thesis, the fine particle number and mass emissions, particle composition and morphology, and gas emissions were investigated from a modern (MMH) and conventional masonry heaters (CMH), sauna stoves (SS) and pellet burner. The investigation was based on laboratory and field experiments applying extensive and unique particle sampling methods. In addition, we obtained a general picture of the significance of different factors influencing the fine particle emissions from RWC appliances.

The appliance type, fuel and operational practices were found to affect clearly the combustion conditions and thus, quantity and quality properties of fine particle emissions from RWC. The measurement methods used have a strong influence on the emission results, particularly on the organic emission and the fraction of coarse particles. In order to get reliable results, the dilution samplers should be applied with small particle losses and a low dilution ratio. Total PM is not a reliable factor for comparison of particle emissions from RWC primarily due to the occurrence of these particles in the flue gas is sporadic and dependent on the combustion appliance, isokineticity is not easy to perform, and there are significant losses of coarse particles in the measurement in all kind of measurement methods.

The fine particles from wood combustion are formed primarily from the pyrolysis gases (EC, i.e. soot and particle organic matter (POM)) and the vaporized alkali metal compounds (i.e. fine ash). In good combustion conditions (e.g. in pellet combustion), the PM_1 emission factors were low, typically below 0.3 g kg^{-1}, and over 90% of the PM_1 consisted of alkali metal compounds. This is because the burners have well controlled combustion process and they are equipped with effective heat exhangers and advanced combustion parameter devices such as an O_2-sensor. The fuel is fed according to the heat demand and combusted at a high temperature in a small grate with staged air.

In batch combustion, the combustion conditions are more incomplete and vary during the different combustion phases. From the CMH the typical PM_1 values were 1.6–1.8 g kg^{-1}, and from the SS 2.7–5.0 g kg^{-1}, but were strongly dependent on operational practices. With an optimal operational technique, the PM_1 from a CMH was as low as 0.6 g kg^{-1}. Respectively, in smouldering combustion the PM_1 emission increased to 10 g kg^{-1}. Fine ash comprised 20–30% of PM_1 from the CMH, whereas PM_1 from the SS was composed mainly of EC (55%) and POM (41%). From smouldering combustion, the percentage of POM even increased: it was 69% of analyzed PM_1, whereas EC comprized 28% of PM_1. The highest emissions were caused presumably by the overall lack of available oxygen which led to incomplete combustion conditions in masonry heaters and sauna stoves with too fast pyrolysis and too high a fuel combustion rate. The high emissions from sauna stoves were also due to the conventional combustion technique with a small firebox and short ducts without significant secondary air supply. Respectively, the good secondary combustion in the MMH reduced the POM and gaseous emissions, but not substantially the EC emission. In the best cases, PM_1 emissions were 0.3–0.5 g kg^{-1}, whereas the typical values are about 0.7–0.8 g kg^{-1}.

The POM and EC correlated very well with the PM_1 emissions, whereas fine ash emission was dependent only on the combustion temperature in RWC. However, the chemical composition of the fuel ash had a strong effect on the release of alkali metals, when the agricultural fuels were compared with wood pellet. The PM_1 emission values from the CMH and pellet appliances were well comparable with those reported in other studies, whereas the PM_1 emissions from the MMH were lower, and those from the SS mainly higher, than in other batch combustion studies.

In the submicron range, the mass size distribution was uni- or bimodal depending on combustion conditions. In some cases, there was also an indication of a supermicron mode at around 1–5 µm particle diameter. The mass mean diameter (MMD) was about 160 nm from pellet combustion, 200–300 nm from the normal combustion of the CMH, and over 500 nm in the smouldering combustion of the CMH.

On average, there were no clear differences in number emissions between different appliances and they did also not correspond with the completition of combustion. The particle number emission were high, varying from 1.0×10^{14} kg^{-1} to 42×10^{14} kg^{-1}. The particle number distributions were mainly dominated by ultrafine (<100 nm) particles, but varied dependent on combustion conditions. The occurrence of the nucleation mode in RWC is very rare. In the wintertime field experiments we observed that the nucleation of organic compounds does not occur in the firebox but rather in the chimney when, in addition to smouldering combustion, the prevailing physical conditions in the flue gas are favourable.

The particle number emission was related to the particle size in such a way that incomplete combustion produced lower number emissions but larger particle sizes than more complete combustion. According to parallel particle size distribution and morphology measurements in this study, it seems that the released ash particles may play an important role in the formation of the particle number emission in RWC. In the CMH experiments, the ultrafine mode in the particle number distributions seemed to be determined mainly by the amount of released ash forming material in combustion. Respectively, the shifting of particle size during different combustion conditions seemed to be determined by the amount of condensed organic vapour in the flue gas. Thus, it seems that the released ash particles may play an important role in the formation of the particle number emission also in incomplete combustion conditions. Generally, the morphology of RWC particles is very complex and varies remarkably between different combustion conditions and thus, more information is yet needed.

Controlling the gasification rate via the primary air supply, log and batch size, as well as fuel moisture content, is important for the reduction of emissions in batch combustion appliances. For good combustion quality, short charging intervals with small batch size are required. To reduce emissions of sauna stoves, the combustion technique or secondary removal techniques must be developed. In good combustion, the release of alkali metals may be reduced with the use of a suitable mixture of pellet fuels. In addition, the size of pellet combustion units with pilot flames should be such that continuous combustion is probable. If this is not possible, these appliances should also be equipped with heat storage tanks.

This thesis provided detailed information about fine particle emissions from RWC which can be used in the development of combustion techniques that produce fewer fine particles, and also as the scientific base for further studies. The results can also be used to exploit the development of secondary removal techniques for small scale biomass combustion and the determining of measurements standard for particle measurement from RWC. In addition, the uncertainty ranges produced can be exploited in emission inventories. In future, the harmfulness of different types of particles should also be studied: in particular, the health effects of fine ash particles should be determined. Also basic research on particle formation mechanism on specific combustion conditions will be even needed.

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APPENDIX I: EMISSION FACTOR TABLES.

Table 1. Fine particle number (N) emission factors ($\times 10^{14}$ # kg^{-1}) and particle geometric mean size (GMD, nm) measured in this study (**I–IV**) and other studies.

	This study				Other studies	
	N (ELPI)	**N (FMPS)**	**GMD_{ae} (ELPI)**	**GMD_{em} (FMPS)**	**N (ELPI)**	**N (SMPS/DMPS)**
Pellet burners and boilers	8.1[IV]	9.5[IV]	62[IV]	51[IV]	0.95[a], 1.5–2.7[b]	4.9[c]
Pellet burner, agricultural fuels	6.3–8.4[IV]	10–11[IV]	58–81[IV]	52–44[IV]		
Pellet stoves					6.7[d], 8.7[e]	16[c]
Stoker burners, wood pellets					1.0[f], 2.4[g]	
Stoker burners, wood chips					1.7[g], 2.1[f], 6.5[h]	17[c]
Wood log boilers					3.8[i]	11[c]
Modern masonry heater	5.9[I], 8[III]	7.3[III]	83[III]	75[III]	1.3–3.4[f]	
Conventional masonry heater	3.1[I], 3.9[II], 27–31[III]	3.9[II], 12–26[III]	65[II], 49–75[III]	56[II], 54–76[III]	24–42[h]	28[c]
Wood stoves	17[III]	9[III]	53[III]	66[III]	2.8–7[f]	4.0[j], 9.9[c]
Sauna stove	12[III], 18[I]	12[III]	114[III]	106[III]	9.8–17.5[h]	

*****From smouldering combustion of CMH, N (ELPI) was 1.9×10^{14} # kg^{-1}, N (FMPS) 1.4×10^{14} # kg^{-1}, GMD_{ae} 160 nm and GMD_{em} 118 nm (**Paper II**). [a]Tissari *et al.*, 2004b; [b]Johansson *et al.*, 2004; [c]Gaegauf *et al.*, 2001; [d]Tissari *et al.*, 2004a; [e]Sippula *et al.*, 2007a; [f]Tissari *et al.*, 2005a (values are from single measurements in PIPO project); [g]Tissari et al., 2004b; [h]Tissari *et al.*, 2007 (values are from VTTs PUPO field measurements); [i]Tissari *et al.*, 2005b; [j]Hedberg *et al.*, 2002.

APPENDIX I: EMISSION FACTOR TABLES (CONT.)

Table 2. Fine particle mass (PM_1) and total particle mass (PM) emission factors (g kg^{-1}) measured in this study (**I–IV**) and other studies from raw and diluted flue gas.

	This study From diluted gas **PM_1**	**Other ref.** From diluted gas **PM_1**	**Other ref.** From hot flue gas **Total PM**
Pellet burners and boilers	0.28[IV]	0.18[a]	0.2–0.42[a,b,c]
Pellet/stoker burners, agricultural fuels	0.3–0.5[IV]		1.48[d]
Pellet stoves		0.2–0.36[e], 1.9–4.0[f]	1.0[b]
Stoker burners, wood pellets		0.19[g], 0.22[h]	0.16[h], 0.25[g]
Stoker burners, wood chips		0.24–0.35[h,g,i]	0.52[d], 0.37–0.40[h,g], 1.3–1.7b[,i]
Wood log boilers		1.0[j]	0.5[b], 0.4–0.6[k], 1.7–42[m]
Modern masonry heater	0.7[I,III]	0.3–0.5[g]	1.1–1.2[g]
Conventional masonry heater	0.6–1.6[III], 0.7[I], 1.8[II]	0.7–0.8[n], 1.9[i], 2.5–3.3[o]	1.7–1.9[o], 2.5[f], 3[b], 3.1–9.1[i]
Wood stoves	0.9[III]	0.5–1.2[g], 2.3–10.2[p], 4–9[q], 8.9–13.9[f], 5.1–9.5[r], 1.3[s]	1.3[b], 2.7–3.3[g]
Cookstove		0.9–2.8[t]	2–5[u]
Sauna stove	2.7[III], 5.0[I]	2.9[i]	4.5–10.6[i]

*From smouldering combustion of the CMH, PM_1 was about 10 g kg^{-1} (**Paper II**). [a]Tissari *et al.*, 2004b; [b]Gaegauf *et al.*, 2001; [c]Johansson *et al.*, 2004; [d]Launhardt and Thoma, 2000; [e]Boman *et al.*, 2005; [f]EPA, 1996a (range from different stoves); [g]Tissari *et al.*, 2005a (PM_1 are DLPI values from single measurements); [h]Tissari et al., 2004b; [i]Tissari *et al.*, 2007 (PM_1 are DLPI values from VTTs PUPO field measurements); [j]Tissari *et al.*, 2005b; [k]Johansson *et al.*, 2004 (modern boilers); [m]Johansson *et al.*, 2004 (old boilers); [n]Tissari *et al.*, 2007 (PUPO pilot measurements); [o]Tissari *et al.*, 2007 (PUPO health measurements in summer 2006); [p]Hays *et al.*, 2003; [q]Mcdonald *et al.*, 2000 (total PM in dilution tunnel); [r]Schauer *et al.*, 2001; [s]Hedberg *et al.*, 2002; Jordan and Seen, 2005; [u]Venkataraman and Uma Maweshara Rao, 2001; [v]Oahn *et al.*, 2005.

APPENDIX I: EMISSION FACTOR TABLES (CONT.)

Table 3. CO (g kg^{-1}) and OGC (gC kg^{-1}) emissions factors measured in this study (**I–IV**) and other studies.

	This study*		**Other studies**	
	CO	OGC	CO	OGC
Pellet burners and boilers	0.55[IV]		0.6–2.3[a], 0.4[b]	0.02–0.08[a], 0.04[c]
Pellet burners, agricultural fuels	1.5–1.6[IV]			
Pellet stove			2.5[d], 18–24[e]	
Stoker burners, wood pellets			3.7[f], 7.6[g]	
Stoker burners, wood chips			2.3[c], 6.0–8.8[f], 26[g]	0.1[c]
Wood log boilers			22[h], 10–25[i], 80–300[j]	5.5[h], 0.3–1.7[i], 13–90[j]
Modern masonry heater	14[I], 28[III]	0.4[I]	15–16[g]	
Conventional masonry heater	22[I], 42[II], 29–68[III]	2.7[I], 2.2[II], 1.9–6[III]	67–74[k], 15–16[m], 68[e], 29–56[n]	4.6–6.2[k], 1.1–1.2[m]
Wood stove	35[III]	2.3[III]	25–47[g], 28[o], 47–105[e]	
Sauna stove	55[I], 120[III]	10[I], 13[III]	65–137[n]	

*From smouldering combustion of the CMH, CO was 150 g kg^{-1} and OGC 30 gC kg^{-1} (**Paper II**). [a]Johansson *et al.*, 2004; [b]Tissari *et al.*, 2004b; [c]Launhardt and Thoma, 2000; [d]Sippula *et al.*, 2007a; [e]EPA, 1996a (range from different stoves); [f]Tissari *et al.*, 2004b; [g]Tissari *et al.*, 2005a (values are from single measurements in the PIPO project); [h]Tissari *et al.*, 2005b; [i]Johansson *et al.*, 2004 (modern boilers); [j]Johansson *et al.*, 2004 (old boilers); [k]Tissari *et al.*, 2007 (PUPO health measurements in summer 2006); [m]Tissari *et al.*, 2007 (PUPO pilot measurements); [n]Tissari *et al.*, 2007 (VTTs PUPO field measurements); [o]Koyuncu and Pinar, 2007.

APPENDIX II: CALCULATION OF DR AND EMISSION FACTORS

The raw measurement values were first dilution corrected. The DR was calculated on the basis of the concentrations of CO_2 (dry) in raw and diluted exhaust gas with the equation

$$\mathrm{DR} = \frac{\mathrm{CO}_{2,\mathrm{FG}} - \mathrm{CO}_{2,\mathrm{BG}}}{\mathrm{CO}_{2,\mathrm{D}} - \mathrm{CO}_{2,\mathrm{BG}}}, \quad (1)$$

where $CO_{2,D}$ is the CO_2 concentration in the diluted gas (CO_2-sensor: Sensorex Ltd., Sensorex SX500D IR sensor, or Cemas Gas Analyzing Rack, ABB Ltd.), $CO_{2,FG}$ is the CO_2 concentration in the raw flue gas and $CO_{2,BG}$ is the CO_2 concentration in the background dilution air. In **Paper I** the DR was calculated by the method described in Sippula *et al.*, 2007a.

The dilution was corrected with state correction and the normalised concentration c_n is then

$$c_n(T = 0^o C) = \frac{DR}{V} \times \frac{273.15}{273.15 + T_{s\,T}}, \quad (2)$$

where V is the volume of the sample in its conditions and T_s is the sample temperature.

The nominal emission values (q_e) were calculated in relation to energy input to the combustion process (SFS 5624, 1990) according to the equation (3)

$$q_e = c_n \times \lambda \times k \times Q_s. \quad (3)$$

The air-to-fuel ratio λ is

$$\lambda = \frac{20.9}{20.9 - O_2}, \quad (4)$$

where O_2 is the flue gas oxygen concentration (dry). According to SFS 5624, fuel moisture factor k is

$$k = \frac{H_u}{H_u - H_w} \quad (5)$$

where H_u is the net heating value of dry fuel, and H_w, the amount of heat consumed in water evaporation. H_w is determined

$$H_w = w_v \times l_v = \frac{\gamma_v}{1 - \gamma_v} \times l_v, \quad (6)$$

where w_v is the mass ratio of water and dry substance, l_v is the evaporation heat of water (2.50 MJ/kg in 0 °C) and γ_v is the mass ratio of water and wet fuel. In addition, factor Q_s is the dry volume of the flue gas per energy unit formed in the combustion of dry fuel. O_s is (almost) the same for all the solid fuels and therefore a factor of 0.25 m^3 MJ^{-1} was used in all experiments.

The emission factor in relation to the amount of fuel used in units of g fuel kg^{-1} (dry), q_m, was defined by equation (7)

$$q_m = q_e \times H_u. \quad (7)$$

In biomass combustion studies, the concentration results are presented also as normalized to 10% (continuous combustion appliances) or 13% (batch combustion appliances) oxygen in the dry flue gas. In these cases, cn was multiplied by a factor r, that is

$$r = \frac{20.96 - O_{2,n}}{20.96 - O_2}, \quad (8)$$

where O_2 is the flue gas oxygen concentration (dry), $O_{2,n}$ is normalized O_2 (e.g. 10 or 13%) and 20.96 is the air oxygen concentration.

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